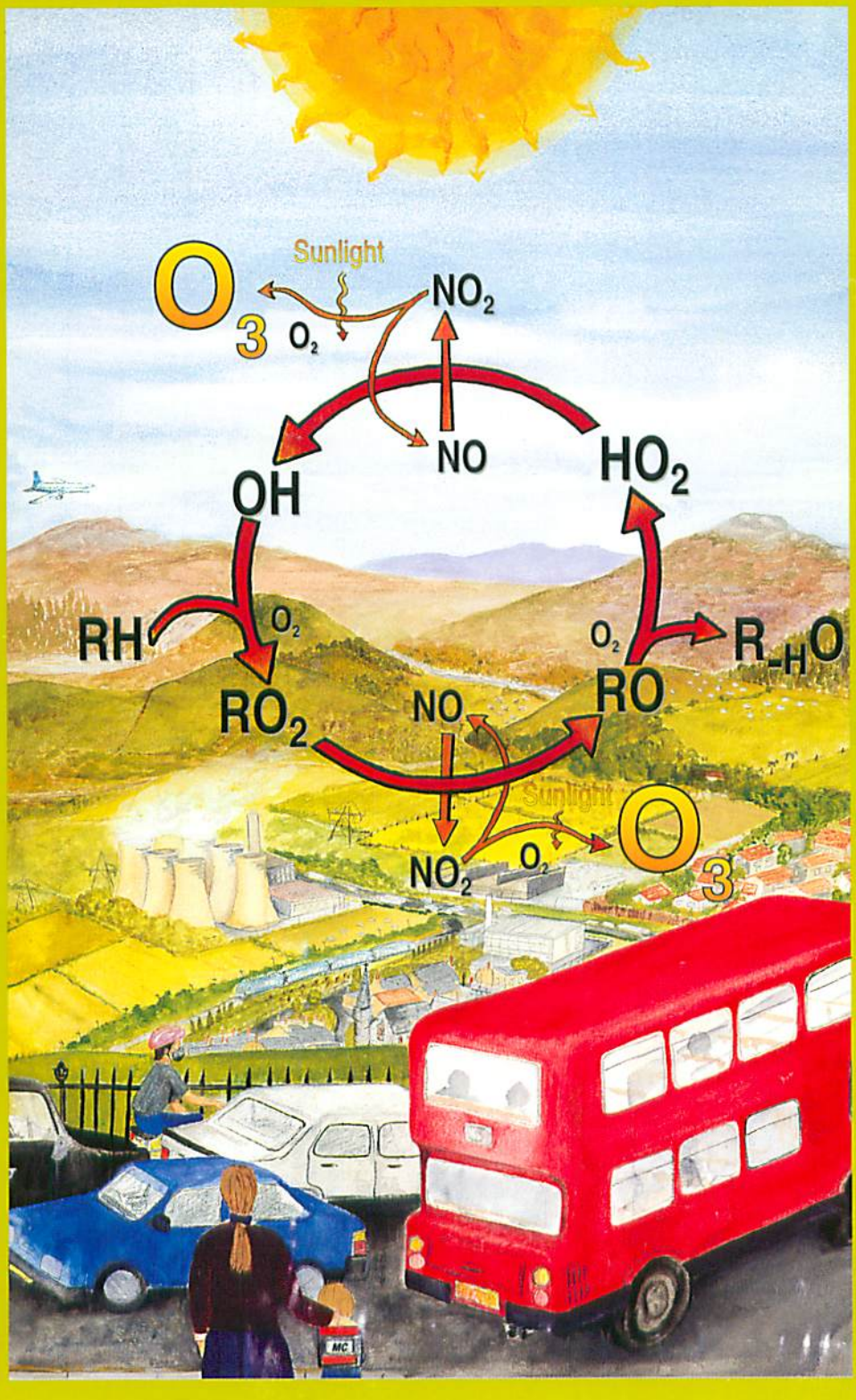
OZONE IN THE UNITED KINGDOM



Prof D. Fowler
Ms M. Coyle
Prof R. Anderson
Dr M.R. Ashmore
Dr J.S. Bower
Ms R.A. Burgess
Dr J.N. Cape
Dr R.A. Cox
Dr R.G. Derwent
Dr G.J. Dollard
Prof P. Grennfelt
Prof R.M. Harrison
Prof C.N. Hewitt
Prof Ø. Hov
Dr M.E. Jenkin
Dr D.S. Lee
Dr R.L. Maynard
Prof S.A. Penkett
Mr R.I. Smith
Mr J.R. Stedman
Dr K.J. Weston
Dr M.L Williams
Dr P.J. Woods

Fourth Report of the Photochemical Oxidants Review Group, 1997

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Further copies available from:

Ms Lucy Moore
Air and Environment Quality Division
Department of the Environment, Transport and the Regions
Room B356
Romney House
43 Marsham St.
London, SW1P 3PY

Ms Mhairi Coyle
Edinburgh Research Station
Institute of Terrestrial Ecology
Bush Estate
Penicuik
Midlothian
EH26 0QB

Technical enquiries to:

Dr M.L. Williams
Air and Environment Quality Division
Department of the Environment, Transport and the Regions
Room B358
Romney House
43 Marsham Street
London, SW1P 3PY

Prof. D. Fowler
Edinburgh Research Station
Institute of Terrestrial Ecology
Bush Estate
Penicuik
Midlothian
EH26 0QB

United Kingdom Photochemical Oxidants Review Group, 1997

Prof D. Fowler (Chairman)	Institute of Terrestrial Ecology
Ms M. Coyle (Secretary and Editor)	Institute of Terrestrial Ecology
Prof R. Anderson	St. George's Hospital Medical School
Dr M.R. Ashmore	Imperial College of Science, Technology and Medicine
Dr J.S. Bower	AEA Technology
Ms R.A. Burgess	University of East Anglia
Dr J.N. Cape	Institute of Terrestrial Ecology
Dr R.A. Cox	University of Cambridge
Dr R.G. Derwent	Meteorological Office
Dr G.J. Dollard	AEA Technology
Prof P. Grennfelt	Swedish Institute of Environmental Research (IVL)
Prof R.M. Harrison	University of Birmingham
Prof C.N. Hewitt	Lancaster University
Prof Ø. Hov	The Norwegian Institute of Air Research (NILU)
Dr M.E. Jenkin	AEA Technology
Dr D.S. Lee	AEA Technology
Dr R.L. Maynard	Department of Health
Prof S.A. Penkett	University of East Anglia
Mr R.I. Smith	Institute of Terrestrial Ecology
Mr J.R. Stedman	AEA Technology
Dr K.J. Weston	University of Edinburgh
Dr M.L. Williams	Department of the Environment, Transport and the Regions
Dr P.J. Woods	National Physical Laboratory

See appendix 1 for contact details.

Photochemical Oxidants Review Group – Terms of Reference

1. The Photochemical Oxidants Review Group is an official body of experts set up by the Department of the Environment to review current knowledge on the physical and chemical aspects of photochemical oxidants and associated precursors. It is a working body and not just a liaison group.

2. The initial goal was to prepare a preliminary review of the photochemical oxidant climate of the United Kingdom, published in February 1987. This was followed by: a review of nitrogen oxides in the United Kingdom in 1990; ozone and nitrogen dioxides in 1993; ozone, nitrogen oxides and volatile organic compounds in 1997.

3. In preparing the above reviews, the group has identified critical areas of uncertainty and recommended where further research, within the overall national effort, is needed.

4. The group makes recommendations for changes to relevant monitoring networks in the United Kingdom.

5. The group provides an informal forum for discussion of research plans and results.

6. The group acts as a point of liaison with relevant international bodies.

EXECUTIVE SUMMARY

This report provides an analysis of UK measurements of ozone and other photochemical oxidants in ground level air primarily for the period 1990 to 1995. In particular the report analyses the spatial patterns of ozone concentration throughout the UK and trends with time to identify the areas, crops and communities subjected to the largest exposure and to show the direction of any trends. The problem of tropospheric ozone is regional, and in some aspects global, and a brief consideration of the relative ozone climates in different parts of Europe is presented to provide the necessary perspective for the assessment.

In this executive summary the key findings from the individual chapters are drawn together to provide a snapshot of the current problem of ground level photochemical oxidants in the UK. It is clear from the analysis that ozone concentrations represent a major phytotoxic air pollutant throughout the UK (in common with the rest of Europe and N. America). Ozone also represents a potential threat to human health although in this analysis the current scale of human health effects for ozone in the UK does not appear to be very large. Ozone is also responsible for reducing the lifetime of materials, especially coatings and elastomers.

There is some evidence of a decline in the magnitude of peak concentrations during the last decade although no general downward trends in either average concentrations or exceedance of thresholds for effects on vegetation in response to reduced NO_x emission have yet been detected. Detailed maps of ground level ozone concentrations throughout the UK have been derived from the monitoring data; such maps are necessary to quantify the spatial exceedance of thresholds but are subject to considerable uncertainty, especially in polluted and complex terrain.

Ozone Chemistry

- The formation of photochemical ozone results from the sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of the nitrogen oxides, NO_x (= NO and NO_2). The rates and mechanisms of the oxidation of VOCs are generally well characterised and quantified by laboratory study, although some significant uncertainties remain for particular classes of VOC (e.g. aromatic hydrocarbons and terpenes).
- The chemistry interconverting oxidised nitrogen compounds is reasonably well understood, and explains the formation of a range of inorganic and organic species which can act as reservoirs for NO_x and hydrogen-containing free radicals. At night, the nitrate radical (NO_3) plays a central role in the chemistry of oxidised nitrogen species.
- Certain chemical reactions in the condensed phase, either on surfaces or in liquid droplets, may influence the concentrations of key species involved in the gas phase mechanisms and are as yet poorly understood.

Ozone Concentrations in the UK

- The UK has a rural network of 17 stations and an urban network of 36 (1/5/97) stations which provide the broad regional spatial patterns in O_3 concentrations throughout the country and the concentrations in representative urban areas respectively.The data are freely available to the public and distributed by CEEFAX/TELETEXT, a freephone number and the INTERNET (details in Table 3.2 and Appendix 2).
- The annual mean ozone concentrations in the UK vary between regions and with topography. The largest mean concentrations occur in rural areas, and in all areas mean concentration increases with altitude. The low altitude (< 200 m) concentrations are largest along the south coast of England.
- Annual mean ozone concentrations are generally lower in urban areas, by on average 20% to 40% of the nearby rural concentration, representing a 5 to 10 ppb reduction.
- Ozone concentrations are, on average, larger at the coast by about 20%, the effect being restricted to the area within 5 to 10 km of the coast.
- There are clear annual and diurnal cycles in ozone concentration in the UK (and elsewhere in Europe) with a spring maximum and an autumn minimum and mid afternoon peak and nocturnal minimum respectively.
- Concentrations of ozone exceed thresholds for effects on vegetation and human health throughout the UK. The largest and most frequent exceedances occur in southern England and especially in rural areas of SE England.
- Maps of mean ozone concentrations and the thresholds for effects on vegetation and human health have been constructed for the UK. The maps are subject to considerable uncertainties as a consequence of the limited number of monitoring stations and the complexity of the landscape.
- These maps show exceedance of critical levels for effects on vegetation over large areas of the UK (detailed in the summary of effects in Chapter 7.1 and in Section 3.4).
- Maps of the average exceedance of the EPAQS ozone standard (8 hour running mean over 50 ppb) from 1990 to 1995 show exceedance of the 97th percentile threshold throughout approximately 98% of the UK.
- Trends in annual mean O_3 concentration are significantly positive (at the 5% level) at 9 sites. At sites which are appreciably influenced by local pollutant sources, the trend is negative but small and variable, averaging -0.1% per year.
- The magnitude of peak concentrations has declined, with the average monthly peak concentration during the period 1986 to 1995 being 20 ppb to 30 ppb smaller than during the period 1972 to 1985 and the monthly 95th percentile showed a decline averaging

0.8 ppb per year. This is a very important improvement in air quality in the UK as the peak concentrations are associated with human health and vegetation effects.

- The exceptionally hot sunny summer of 1995 led to an expectation of peak ozone concentrations similar in magnitude to those recorded during the similarly hot sunny summer of 1976. However, although concentrations were higher than those recorded in recent years, they failed to reach the levels observed in 1976. This was partly due to reductions in emissions of precursor species in some European countries but also to air circulation patterns over Europe and the UK, which frequently brought relatively clean air into the UK from N. Europe.
- The main sink for ozone in the UK is dry deposition to the ground, which over the year represents a total of *ca* 1500 kt O_3 over the country.
- In urban areas, the removal of O_3 by reaction with NO represents a further sink for O_3. The depletion of O_3 in the UK is greater on average than the photochemical production, so that at the downwind coast, the concentrations are generally smaller than those upwind. On a larger scale the photochemical production of O_3 and other oxidants in the UK 'plume' downwind of the coast extends over several hundreds of km.
- Peak concentrations of ozone are positively associated with other pollutants such that during periods with concentrations of ozone in excess of 60 ppb, the concentrations of SO_2 and NO_2 are also substantially larger than their mean values.

Other Photochemical Oxidants

- Peroxyacetyl nitrate (PAN), hydrogen peroxide and nitric acid are the most important products of photochemistry besides ozone, but none are thought to reach damaging concentrations in Britain.
- Hydrogen peroxide concentrations measured at Harwell, Oxfordshire, between 1992 and 1994 show no evidence of a long-term trend since 1988. Average concentrations were 0.2-0.3 ppb, with hourly maximum not exceeding 3 ppb.
- Long-term PAN measurements have been made in eastern Scotland and western Ireland. Annual concentrations (geometric mean) were 50-100 ppt in Scotland and 30 ppt in Ireland, smaller than at Harwell (*ca* 175 ppt). The Harwell data showed no long-term trend between 1987 and 1994, although data capture was low in 1992-94.
- PAN concentrations were only correlated strongly with ozone concentrations during photochemical episodes. Large (>0.5ppb) winter PAN concentrations were not always associated with large ozone concentrations.
- PAN episodes in eastern Scotland occurred when anticyclonic conditions brought polluted air from mainland Europe north over England.

Hydrocarbons in the UK

- Total emissions of VOCs in the UK have increased from 2266 kt in 1970 to 2337 kt in 1995. The current inventory indicates that total annual emissions have declined since 1989.
- Mobile sources and solvent usage are the two largest source categories and together account for about 70% of UK emissions of volatile organic compounds.
- Speciated inventories are now available for over 100 VOC compounds.
- Emissions of volatile organic compounds of biogenic origin in the UK were given as 50-100 kt yr^{-1} in the last PORG report. Since then further work has failed to reduce the uncertainty in this estimate, one model predicting less than this and another predicting more.
- The UK has now established a unique national network of hydrocarbon monitoring sites across the UK reporting data hourly on 25 species from 11 urban and 1 rural site.
- Network sites generate data on two carcinogenic compounds, benzene and 1,3 butadiene.
- The UK National Air Quality Strategy has recommended air quality standards for benzene and 1,3 butadiene. Network monitoring data show that current urban concentrations of these compounds are below the standards.
- A complete year of data is available for 1995 and 1996 for most sites and it is apparent that the urban concentrations of the C_2-C_8 hydrocarbons are heavily influenced by motor vehicle emissions and natural gas leakage.
- Local episodes of elevated concentrations are observed at many sites. These are caused by reduced dispersion of local primary emissions of hydrocarbons.
- Measurements of a series of oxygenated hydrocarbons have been made at Harwell, Oxfordshire as part of the EMEP network. Acetone is the most abundant oxygenated hydrocarbon measured and methyl glyoxal the most abundant bi-functional oxygenated organic compound.
- Consideration of rural hydrocarbon measurement data suggest that concentrations may have declined substantially over the period 1970-1990.
- The measured hydrocarbon concentration data have been compared with emission inventories. The automatic measurements point to the national inventory underestimating the emissions of C_2-C_8 hydrocarbons by about 40%.
- Direct, on board measurements of exhaust emissions from motor vehicles are in good agreement with kerbside measurements for all VOCs except acetylene.
- Methane is an important VOC in the atmosphere, making a significant contribution to regional ozone formation. Computer modelling studies have shown that methane accounts for 15-20% of ozone formed photochemically over north West Europe.

- The methane concentrations monitored at Mace Head, Ireland continued to rise up until 1991, when the annual increase slowed somewhat. The increase picked up again in 1994 and 1995; background methane concentrations now stand at about 1805 ppb.
- An analysis has been made of the contributions to photochemical ozone formation which can be sustained by the observed concentrations of 87 individual hydrocarbons reported by the monitoring networks and determined from detailed surveys. The top 10 most important hydrocarbons are i-butene > propene > ethene > isoprene > 1,2,4-trimethylbenzene > m+p-xylene > 1,3,5-trimethylbenzene > *trans*but-2-ene > toluene > *trans*pent-2-ene.
- Biogenic hydrocarbons are unlikely to account significantly for the elevated ozone concentrations observed in the United Kingdom. These will contribute to background ozone concentrations and hence may indirectly influence peak concentrations. Two biogenic hydrocarbons, isoprene and alpha-pinene, have been found to account for 5.5% and 0.4% respectively, of the ozone forming potential of the observed distribution of hydrocarbons in the United Kingdom.

Oxides of Nitrogen

- Emissions of NO_x in the UK peaked in 1990 at 822 kt NO_x-N and in 1994 were 675 kt.
- Most UK NO_x emissions (83%) are exported from the country, as NO_2, by the wind. The deposition of oxidized nitrogen as dry deposited NO_2 and wet deposited NO_3^- of 142 kt N represents 17% of emissions.
- In some large conurbations NO_x concentrations have declined over the last 5 years in line with national emissions (~ -20%). However, NO_2 concentrations in such areas have changed little as they are governed by the supply of O_3 for oxidation of the primary emissions of NO.
- Close to major conurbations there is evidence that rural NO_2 concentrations have increased since the 1980s, and throughout the UK, NO_2 concentrations are substantially larger than SO_2. However, most rural areas show a small decline in NO_2 concentrations over the period 1987 to 1995.
- In urban areas NO_x concentrations exceed the European Commission guide values and NO_2 concentrations exceed the European Union limit values. These exceedances are expected to decline as urban NO_x emissions decline over the next 5 years.
- Epidemiological studies have shown that day to day variations in concentrations of NO_2 are associated with adverse health effects. These studies include both time-series studies of daily hospital admissions and geographical studies comparing lung function in different areas. Although these effects many not be as marked as those associated with ozone and particles they are significant and, from the health standpoint, NO_2 remains an important air pollutant.
- The toxicity of ambient air pollution mixtures characterised by raised concentrations of NO_2 seems greater than that of NO_2 itself at similar concentrations. This apparent anomaly could be explained by associations between NO_2 and other pollutants.
- Studies of the effects of exposure to NO_2 indoors have shown an association between the presence of gas cookers and respiratory symptoms in asthmatic and non-asthmatic subjects, mostly children. More work is needed to identify the causative agent though a number of workers have suggested that NO_2 may be an important factor.
- In a study of an episode of pollution in London in 1991, characterised by high levels of NO_2 and particles, adverse health effects were detected but it was not possible to distinguish between the possible effects of particles and NO_2.
- Because of new knowledge of the important phytotoxic effects of nitric oxide (NO) the present critical level for impacts of nitrogen oxides on vegetation is a combined value for NO plus NO_2 (termed NO_x). The critical level is 30 $\mu g\ m^{-3}$ (NO_2 equiv.) as an annual mean and applies to NO_x for all categories of vegetation.
- Estimates of NO_x distribution have been derived, using urban and rural conversion factors, from mapped values of NO_2. The critical level for effects of NO_x on vegetation is exceeded over 29% of the UK land area, particularly in rural central and southern England, and in and around major urban areas. In areas where the critical level is exceeded there may be adverse direct effects of NO_x on vegetation although the nature of the effects is uncertain. Semi-natural vegetation is potentially the most sensitive to NO_x exposure because it is often limited by the supply of nutrient nitrogen.

Effects of Ozone on Vegetation

- The assessment of environmental risk related to ozone effects on vegetation is currently based around the critical level concept. Critical levels are defined using the AOT40 index – the cumulative exposure over 40 ppb during a growing season.
- Since the last report the knowledge of critical levels for ozone effects on vegetation has greatly improved. At an international workshop in Kuopio, Finland in April 1996, revised critical levels of ozone were agreed to prevent damage to the most sensitive crops, forests, and semi-natural vegetation. This has provided the necessary basis to quantify the spatial patterns of exceedance of these critical levels in the UK.
- Using the assessment method and critical level values recommended at this workshop, the critical level for forests, an AOT40 of 10000 ppb h over six months, is only exceeded in southern Britain. The area in exceedance of the critical level represents 15% of UK land area, and 23% of UK forest area. In contrast, the critical level for crops and semi-

natural vegetation, an AOT40 of 3000 ppb h over 3 months, is exceeded almost throughout England and Wales, and in many parts of Scotland. The area in exceedance of the critical level represents 81% of UK land area, 91% of UK area of arable crops, and 76% of UK area of semi-natural vegetation. There is limited experimental evidence of impacts on vegetation in certain of the areas where the critical level is exceeded.

- Exceedance of the critical level does not mean that there will be damage to vegetation, but only that the risk of damage exists for sensitive species and conditions. Furthermore, the degree of exceedance of the critical level cannot be used directly to estimate the extent of damage to vegetation, or to assess the economic impacts of ozone on vegetation. This is because exposure to high levels of ozone is correlated with high temperatures and irradiances, and high vapour pressure deficits. For example, there is considerable variation between years in the AOT40 values found in the UK, but the years with high values of AOT40, and wider exceedance of the critical level, are often the hotter and drier years in which accumulated soil moisture deficit is greater, and hence ozone uptake by vegetation is lower.
- AOT40 values are calculated over a fixed three or six month growing period, but this may not reflect actual UK growth periods. Furthermore, the ozone sensitivity of vegetation is not constant, but varies with the stage of plant development. The timing of ozone episodes varies between years and sites in the UK, and this will significantly alter the impact on vegetation.
- Analysis of the seasonal patterns of AOT40 across the UK shows large variations from year to year. Data averaged over several years showed a more consistent pattern:- in April and May, there was relatively little difference in AOT40 values across the UK, but for the rest of the summer months, there was a large gradient from southern sites, where large additional AOT40 exposures occurred, to remote northern or western sites, at which almost no additional AOT40 exposure occurred.
- Recent studies have shown large gradients in AOT40 values between the standard measurement height of the monitoring network, and the height of the vegetation, in the case of crops and semi-natural vegetation. This means that exceedance of the critical level estimated using the national network may significantly overestimate the true area of exceedance in the UK.
- There is an urgent need to estimate more accurately the real impact of ozone on vegetation in areas of the UK where the critical level is exceeded. This will require further experimental and modelling work, so that the effect of factors such as variation in sensitivity between species, the effects of climatic and edaphic factors, and the timing of ozone episodes, can be quantified. A key focus of this work will be the development of methods to map the uptake of ozone by vegetation, and to quantify the relationship between this uptake and observed effects.
- Within the UK vegetation effects assessment it has not been possible to modify the maps of AOT40 for the urban reduction in exceedance.

Effects of Ozone on Materials

- Ozone has a damaging effect on certain materials, including polymers, rubbers, surface coatings and textiles. In combination with N- and S- pollutants it has been shown to corrode metals and with S-compounds damage some types of stone.
- Material damage is related to the annual mean ozone concentration, which is lowest in urban areas where the density of at-risk materials is highest .
- A preliminary critical level for material damage was set at 20 ppb as an annual average concentration, at a UNECE workshop in 1993. This level is currently exceeded in all of the UK with the exception of some urban areas.
- Estimates of the current cost of damage are of the order of several £100 million for the UK. However the methods used to produce these estimates are very uncertain and can only give an indication that the costs are substantial.
- As measures to control the emissions of VOCs and NO_x come into effect, ozone levels may rise in urban areas with an associated increase in the cost of damage to materials.

Effects of Ozone on Human Health

- Ozone is the most irritant of the common air pollutants and exposure to concentrations commonly encountered in the UK has been shown to produce inflammation of the respiratory tract.
- In terms of effects on standard physiological indices of lung function there is no evidence to suggest that asthmatic subjects are more sensitive to ozone than other individuals. However there is evidence based on studies of the inflammatory response to the airways induced by exposure to ozone to suggest that asthmatic subjects are a little more sensitive than others.
- The combination of ozone and acid aerosols may have a more marked effect than exposure to ozone alone.
- Long term exposure to ozone in the USA at average concentrations greater than those encountered in the UK has been shown to be associated with a chronic decline in lung function.
- A recent study has demonstrated that ozone levels in London are associated with changes in daily mortality rates. Cardiovascular and respiratory mortality were affected with the effects being most marked during the summer season.
- Recent time-series studies of the effects of daily variations in concentrations of ozone and indices

of ill-health including hospital admissions and mortality have shown that there may be a threshold of effect at about 40-60 ppb ozone, 8 hour average concentration.

- Depending on the assumptions made about thresholds of effect for ozone, a wide range of hospital admissions related to ozone could be derived. These range from 0.35% to 6.1% of total admissions for respiratory disorders. The Department of Health Committee on the Medical Effects of Air Pollutants will investigate this further and report later in 1997.
- Because admission to hospital for respiratory disease is a relatively rare event, the effect of ozone on hospital admissions, already small in relative terms, is likely to have only a small public health impact. However, panel studies indicate that ozone also increases the risk of a worsening of symptoms or increased medication requirement. Although this is a small relative effect, a large number of people are at risk and when the widespread exposure to ozone is also taken into account, the health impact of increased ozone levels is likely to be greater than the effect on hospital admissions suggests.
- New evidence from the UK and from elsewhere confirms the conclusions of the Department of Health Committee on the Medical Effects of Air Pollutants that, at the population level, air pollution has a detectable but relatively small effect on the provocation of existing asthma, and is unlikely to play a role in the incidence of new asthma.

Ozone in a European Perspective

- Ozone is the major gaseous pollutant throughout Europe and ambient concentrations regularly exceed thresholds for effects on vegetation and human health during the summer in most countries.
- The magnitude of exceedance of effect thresholds for both crops and human health increases along a gradient from the UK towards central Europe. In this respect the UK, along with the Scandinavian countries, are the areas least affected by episodes of elevated ozone in Europe.
- The transport distances of pollutants and their precursors and timescales for chemical production of ozone lead to long range transport of ozone and other photochemical oxidants throughout Europe. As a consequence we share the same air and its associated pollutants. Policies to reduce the frequency and magnitude of elevated ozone episodes require control measures throughout Europe.
- Policies to reduce the Northern hemisphere tropospheric background ozone concentration requires control measures throughout the Northern hemisphere.
- The European ozone monitoring data (1980 - 94) show no consistent trends in mean concentrations throughout the period. A small reduction in mean concentrations has been reported for the Netherlands, although the underlying cause is unclear.

Photochemical Oxidants and the Effects of Emissions Controls

- Regional scale ozone formation and its control is an important policy issue in a number of international policy fora, including in particular, the UN ECE and the European Union.
- The work of the UN ECE has concentrated mainly on the impacts of ozone on crops and trees and has introduced the concept of AOT40 to characterise critical exposure levels of ozone. It is likely that reductions in NO_x and hydrocarbon emissions approaching the maximum feasible will be required if these critical levels are not to be exceeded in future years across Europe.
- The work of the European Union has focused mainly on human health effects and the role played by motor vehicles and their fuels in the deterioration of urban air quality. Proposals are being drawn up for emission and fuel quality standards for the year 2000 and beyond. The Commission have adopted an air quality objective of 90 ppb, 99-percentile hourly mean ozone concentration, a level which is not normally exceeded in the United Kingdom except in the most photochemically active summers.
- The National Air Quality Strategy has set a challenging health-based provisional air quality objective for the UK of 50 ppb as an 8-hour rolling mean expressed as a 97th percentile. VOC and NO_x emission reductions approaching the limits of technical and economic feasibility will be required, going far beyond current policies, if the ozone air quality objective in the National Air Quality Strategy is to be met in the future.
- Further consideration will need to be given to background tropospheric ozone if strict vegetation-based environmental criteria expressed in AOT40 terms are not to be exceeded in the UK and in the rest of Europe. This will require action on ozone precursor emissions at a global scale.

CONTENTS

INTRODUCTION

Over the last three decades the pollutants which characterise the chemical composition of the atmosphere over the UK have changed substantially. In the post-war decade, sulphur dioxide and coal smoke were the major pollutants, and were responsible for substantial effects on human health in UK cities. The Clean Air Act led gradually to cleaner air in our cities, at least for the pollutants derived from coal combustion, and the development of large, coal burning power stations in rural areas with tall stacks minimised the local ground level SO_2 concentrations. Emissions of sulphur dominated the "pollution climate" and associated problems of long range transport and ecosystem acidification were the air pollution issue of the 1970s and 1980s. The problems of acid deposition have not yet been solved, but policies are in place to reduce the deposition of acidity throughout Europe and important progress has already been made. By contrast, the photochemical oxidants and ozone in particular have become major regional atmospheric pollutants throughout the UK and Europe. Even in cities, where ozone concentrations are generally smaller than in rural areas, the major pollutants are from motor vehicles (oxides of nitrogen NO and NO_2 and Volatile Organic Compounds) which are the precursor compounds for ozone production.

Ozone is a natural component of the atmosphere in the stratosphere, where it is produced following the photolysis of molecular oxygen, at altitudes of about 20 km where it intercepts incoming solar UV radiation. Ozone is also present in the troposphere where it plays an important role in the chemical processing of trace gases, pollutant and natural. However, concentrations of stratospheric ozone have declined in polar regions and in the Antarctic spring in particular (Farman *et al*, 1995) while concentrations of tropospheric ozone have increased, especially in the mid-latitude Northern Hemisphere. There are therefore two distinct, very different and largely unrelated problems of atmospheric ozone. The subject of stratospheric ozone lies outside the remit of this review group and the reader is referred to the report of the Stratospheric Ozone Review Group (SORG 1996) for further details.

Ozone in the troposphere is produced through photochemical processes from the oxides of nitrogen (NO_x) and Volatile Organic Compounds (VOCs) the chemistry of which is considered in detail in Chapter 2. Both groups of compounds are emitted by natural processes, in soils and vegetation respectively. However, the large emissions of these gases through combustion, especially by motor vehicles and industrial processes, has led to a large increase in tropospheric ozone at a regional scale and, especially in the mid-northern latitudes, also at a global scale. In the UK for example, the anthropogenic emissions of NO_x are about 40 times the emissions of NO_x from soils. There is strong evidence in the mid-northern latitudes that the current annual average ambient ozone concentrations are about double those in the same zone at the end of the last century (Voltz and Kley, 1988). In addition to the mean value, the peak concentrations in the industrialized countries commonly reach 80 ppb to 120 ppb, concentrations that were not observed in the early measurements. Many of the very large cities of the world (those with populations in excess of 2,000,000) currently experience problems of photochemical oxidants. In some cases the problems are chronic, with exceedances of health thresholds most days of the year.

The problems associated with elevated ozone concentrations range from reductions in crop yields and effects on human health of sensitive individuals to reductions in the lifetime of a range of materials. Ozone is also a greenhouse gas with absorption bands at infra-red wavelengths and is closely linked with the oxidation of a range of atmospheric trace gases and pollutants through its role in the atmospheric chemistry of the OH radical.

Clearly therefore, tropospheric ozone is an important pollutant nationally and internationally with consequences for human health and crop yields among other targets. For these reasons, national governments of Europe are currently negotiating a protocol to control the emissions of one of the main precursor gases, nitrogen dioxide. The introduction of catalytic converters on motor vehicles, to reduce the emissions of both NO_x and VOCs, makes an important contribution to the control of photochemical oxidants, but the process of developing control strategies requires a thorough analysis of the scientific issues, and the effect of different control strategies to be understood.

The approach adopted within the UNECE (United Nations Economic Commission for Europe) to quantify the current ozone problem is the "critical levels" approach in which the maximum dose of ozone to which ecosystems may be exposed without damage to

sensitive organisms is defined and this allows the exceedances of that threshold to be quantified in space and time. The control strategy is then developed to maximize the areas in which critical levels are not exceeded for a given investment in control measures. This procedure is also useful to show the size of emission reductions which would be required to eliminate exceedances of critical levels entirely and the likely timescale of the process. However, there are many uncertainties in the methodology. We cannot be sure that the most sensitive species have been identified and it is difficult to quantify the relative importance of a range of effects which operate over very different time and spatial scales. For this reason "according to current knowledge" is usually added as a rider to the critical levels methodology to highlight both the uncertainty and the fact that the analysis is likely to change as results of new research become available.

To maximize the improvement in air quality in the regions where the effects are being experienced, it is necessary to quantify emissions of precursor gases, define the current average and peak concentrations, specify the relationships between ozone concentration or dose and the biological response, and identify the areas in which exceedances of effects thresholds are occurring. It is also necessary to understand the relationships between emissions of precursors and gas concentrations, which requires an understanding of the chemical mechanisms and their interaction with meteorological variables.

The first PORG Report in 1986 analysed the very limited ozone data available for the UK, and showed that episodes of high ozone concentrations (> 60 ppb), were not uncommon in the summer in the UK, but that too few sites were available to define the spatial patterns in concentrations throughout the country. Following a similar report on the available UK NO_x data, a network of rural monitoring stations was established and the first UK maps of mean ozone concentration became available in 1990 (PORG, 1990). These maps included estimates of exceedances of thresholds for effects on crops and the first evidence of trends in both NO_x and O_3 concentrations in the UK.

The current report provides a thorough analysis of the spatial ozone exposure, and evidence for trends over the eight years of measurements available. In addition, this report describes the current understanding of photochemical oxidants, and ozone in particular, in the UK. We have examined the available monitoring data and recent research in the UK and elsewhere, especially within Europe, to provide the material for review. The terms of reference of the review group are provided in Appendix 1. The available information includes rural and urban monitoring networks to provide the basic measurements of ozone concentration. However, because the ambient concentrations of ozone vary so much in time and space, it is necessary to draw on a range of basic and applied research to provide an up-to-date assessment of the current concentrations, their spatial distributions and trends, and an assessment of the exceedances of thresholds for effects on human health, crops, natural vegetation and materials. The focus of the report is on ozone in the UK but as the problem of photochemical oxidants is regional and global as well as national, the data for the UK are considered in the context of the European ozone problem. The report also briefly considers photochemical oxidants other than ozone, including nitrogen dioxide (NO_2), hydrogen peroxide (H_2O_2), peroxyacetylnitrate (PAN) and nitrous acid (HNO_2).

References

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2. THE CHEMISTRY OF SECONDARY POLLUTANT FORMATION

- The production of secondary photochemical pollutants in the troposphere occurs by sunlight-initiated mechanisms, driven by reactions of reactive free radical intermediates. The chemistry leading to the formation of those secondary pollutants which are routinely measured (ie. ozone, hydrogen peroxide and peroxyacetyl nitrate) is well understood.
- The formation of photochemical ozone results from the sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of the nitrogen oxides, NO_x (= NO and NO_2). The rates and mechanisms of the oxidation of VOCs are generally well characterised and quantified by laboratory study, although some significant uncertainties remain for particular classes of VOC (e.g. aromatic hydrocarbons and terpenes).
- The chemistry interconverting oxidised nitrogen compounds is reasonably well understood, and explains the formation of a range of inorganic and organic species which can act as reservoirs for NO_x and hydrogen-containing free radicals. At night, the nitrate radical (NO_3) plays a central role in the chemistry of oxidised nitrogen species.
- Certain chemical reactions in the condensed phase, either on surfaces or in liquid droplets, may influence the concentrations of key species involved in the gas phase mechanisms.

2.1 Introduction

Although some trace gases emitted into the troposphere present a health risk in their own right, a major additional impact results from their oxidation in the troposphere, which leads to a range of secondary oxidised products, many of which are potentially more harmful than their precursors. Since much of the chemistry is driven by the presence of sunlight, the oxidised products are commonly referred to as *secondary photochemical pollutants*, and include photochemical oxidants such as ozone. The purpose of this chapter is to provide a comparatively detailed description of our current understanding of the chemical mechanisms leading to the generation of secondary photochemical pollutants in the troposphere. Much of the chapter is devoted to a discussion of the gas-phase photochemical transformations of nitrogen oxides and volatile organic compounds, and their role in the formation of ozone. The chemistry producing other oxidants and secondary pollutants (e.g. hydrogen peroxide and peroxy acetyl nitrate) is also described. Some discussion of night-time chemistry and the formation and role of aerosols in tropospheric chemistry is also given, since these are influenced by the gas-phase photochemical processes. Where possible, the processes described are illustrated by observational data.

2.2 The Photochemical Transformations of Oxidised Nitrogen Species

2.2.1 Daytime Interconversion of NO and NO_2

Nitrogen oxides are released into the troposphere from a variety of biogenic and anthropogenic sources (Logan, 1983; IPCC, 1994; Lee *et al*, 1997). Approximately 40% of the global emissions, and the largest single source, results from the combustion of fossil fuels, which almost exclusively leads to emission directly into the planetary boundary layer, mainly in the form of NO. A small fraction (generally ≤10%) may be released as NO_2 (see Chapter 6), or produced close to the point of emission from the termolecular reaction of NO with O_2:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (1)$$

The rate of this reaction is strongly dependent on the NO concentration. Thus, at high levels typical of those close to points of emission, the rate of conversion of NO to NO_2 is rapid (e.g. *ca* 0.5% s^{-1} at 1000 ppm NO), but the significance of reaction (1) decreases dramatically as NO is diluted, with a fractional conversion rate of only 5×10^{-6} s^{-1} at 1 ppm NO. Under most tropospheric conditions, reaction (1) is insignificant, and the dominant NO to NO_2 conversion route is the reaction of NO with O_3 (see Figure 2.1):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2)$$

At a typical boundary layer concentration of 30 ppb O_3, this reaction occurs on a time scale of *ca* 1 minute. During daylight hours, however, NO_2 is converted back to NO as a result of photolysis, which also leads to the regeneration of O_3 as follows :

$$NO_2 + \text{sunlight} \rightarrow NO + O \qquad (3)$$

$$O + O_2 (+M) \rightarrow O_3 (+M) \qquad (4)$$

Thus, reactions (2)-(4) constitute a cycle with no net chemistry. In the absence of competing interconversion reactions, this cycle leads to a "photostationary state" in which the concentrations of NO and NO_2 are related to the O_3 concentration by the following expression (Leighton, 1961),

$$[O_3] = (J_3[NO_2]/k_2[NO]) \qquad (i)$$

where J_3 is the rate of NO_2 photolysis, and k_2 is the rate coefficient for the reaction of NO with O_3. As a result of this rapid interconversion, the behaviour of NO and NO_2 is highly coupled, and they are usually collectively referred to as NO_x. The lifetime of NO_2 with respect to photolysis in the boundary layer depends on latitude, season and time of day. The measured diurnal variation of J_3 shown in Figure 2.2 (latitude 55°N; midsummer clear sky conditions) indicates that the minimum lifetime of NO_2 under conditions typical of the UK is of the order of 1 minute, with a mean daylight lifetime of *ca* 3 minutes. In the wintertime, this is typically a factor of two or three longer.

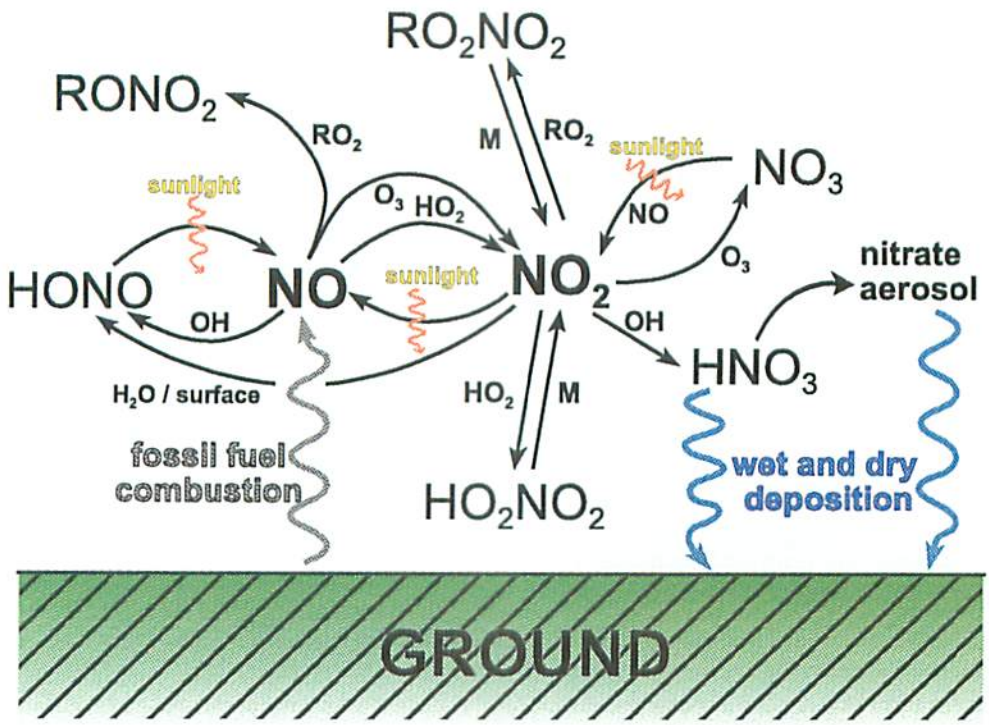

Figure 2.1 Daytime interconversions of oxidised nitrogen compounds in the troposphere.

Other daytime chemical processes interconverting the NO_x species generally involve free radicals. Of particular importance are the hydroperoxy radical (HO_2), and organic peroxy radicals (RO_2), which are mainly produced in the troposphere as intermediates in the photochemical oxidation of carbon monoxide (CO) and volatile organic compounds, as will be described in Section 2.3. Both HO_2 and the RO_2 radicals provide additional NO to NO_2 conversion routes to supplement reaction (2):

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5)$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (6a)$$

However, since conversion of NO to NO_2 as a result of these reactions does not consume O_3, the subsequent photolysis of NO_2 (reaction (3)), followed by reaction (4), represents a net source of O_3. These reactions form the core of photochemical O_3 production in the troposphere for which NO_x, organic compounds and sunlight are essential ingredients, as will be discussed further in Section 2.3. The net production rate of O_3 resulting from this *fast photochemistry* is given by the expression:

$$d[O_3]/dt = (k_5[HO_2]+\Sigma k_{6a}[RO_2])[NO] \quad (ii)$$

The production rate is very variable, since the peroxy radical concentration is a strong function of factors such as location, season, time of day and cloud cover. However, for an ambient NO concentration of 2 ppb (typical of a UK rural site) and a total peroxy radical concentration of *ca* 10 ppt, which has been observed in the UK under summertime conditions (Clemitshaw *et al*, 1997), an O_3 production rate of the order of 10 ppb hr^{-1} may be calculated.

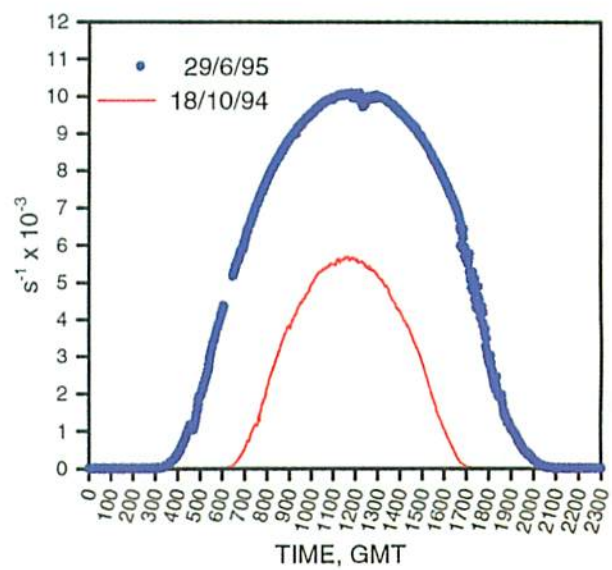

Figure 2.2 Diurnal variation of the NO_2 photolysis rate, J_3, measured at the Weybourne Atmospheric Observatory, Norfolk in midsummer (29th June 1995) and wintertime (18th October 1994), with clear sky conditions (data supplied by K.C. Clemitshaw).

Reactions (5) and (6a) also perturb the photostationary state, and observed deviations from equation (i) are therefore often interpreted in terms of the presence of significant concentrations of the peroxy radicals. A modified equation allowing for deviations can be defined as follows,

$$[O_3] + \Psi_{ox} = (J_3[NO_2]/k_2[NO]) \qquad (iii)$$

where "Ψ_{ox}" represents the observed deviation, which

is usually termed the *missing oxidant* and is effectively the ambient level of oxidising free radicals expressed as an "ozone equivalent" concentration. If the observed deviation is a consequence of reactions (5) and (6a), then:

$$\Psi_{ox} = \{(k_5[HO_2]/k_2)+(\Sigma k_{6a}[RO_2]/k_2)\} \quad \text{(iv)}$$

and the net O_3 production rate is $k_2[NO]\Psi_{ox}$. An example of data showing deviations from photostationary state is given in Figure 2.3. Ψ_{ox} shows a diurnal variation consistent with that expected for photochemically derived free radicals and, for this dataset, its capacity for oxidising NO to NO_2 is comparable with that of O_3 for a significant part of the day. Where simultaneous measurements are available, Ψ_{ox} usually shows a positive correlation with the total ambient concentration of peroxy radicals, $[HO_2] + \Sigma[RO_2]$, measured using the chemical amplification technique (e.g. Cantrell *et al,* 1993). However, the precise calculation of the total peroxy radical concentration from measurements of Ψ_{ox} using equation (iv) is often not possible, since the value of k_{6a} depends on the structure of the RO_2 radical, with currently measured values for a variety of radicals covering a range of more than an order of magnitude (e.g. Sehested *et al,* 1993). It is also possible that deviations from equation (i) result from reactions other than (5) and (6a) (e.g. see Calvert and Stockwell, 1983).

Other chemical transformations of NO_x lead to the generation of a variety of inorganic and organic oxidised nitrogen compounds. Oxidised nitrogen species of atmospheric significance are usually collectively referred to as "NO_Y", which is taken to consist of NO, NO_2, the higher oxides (NO_3 and N_2O_5), the oxyacids (HNO_3, HO_2NO_2 and HONO), the organic peroxy nitrates (RO_2NO_2), the organic nitrates ($RONO_2$) and aerosol nitrate. The component of NO_Y excluding NO and NO_2 is sometimes defined as "NO_Z" (Colvile *et al,* 1996). Most of these species are generated during daylight, and their formation and removal chemistry is described in the subsections which follow. The significance of the formation of the higher oxides (NO_3 and N_2O_5) is greatest for night-time tropospheric chemistry, and is therefore discussed in Section 2.4.

2.2.2 The Formation and Removal of Oxyacids of Nitrogen

The reactions of the NO_X species with HO_X radicals (OH and HO_2) lead to the generation of the oxyacids, nitric acid (HNO_3), peroxynitric acid (HO_2NO_2) and nitrous acid (HONO). The reaction of OH with NO_2 to form HNO_3 is of particular importance, since it provides the predominant chemical removal route for NO_X during daylight, and therefore plays a major role in controlling its concentration:

$$OH + NO_2 (+M) \rightarrow HNO_3 (+M) \quad (7)$$

The boundary layer lifetime of NO_2 with respect to this reaction is *ca* 1 day for a typical background OH concentration of 0.04 ppt (10^6 molecule cm^{-3}), but decreasing to *ca* 2 hours for an elevated OH concentration of 0.4 ppt (10^7 molecule cm^{-3}) consistent with a photochemical episode. HNO_3 is therefore usually a significant component of total NO_Y. It is removed comparatively efficiently from the troposphere by both wet and dry deposition, and also by adsorption on, or reaction with, the tropospheric aerosol (see Section 2.6).

The addition reaction of HO_2 with NO_2 leads to the formation of HO_2NO_2 :

$$HO_2 + NO_2 (+M) \leftrightarrow HO_2NO_2 (+M) \quad (8)$$

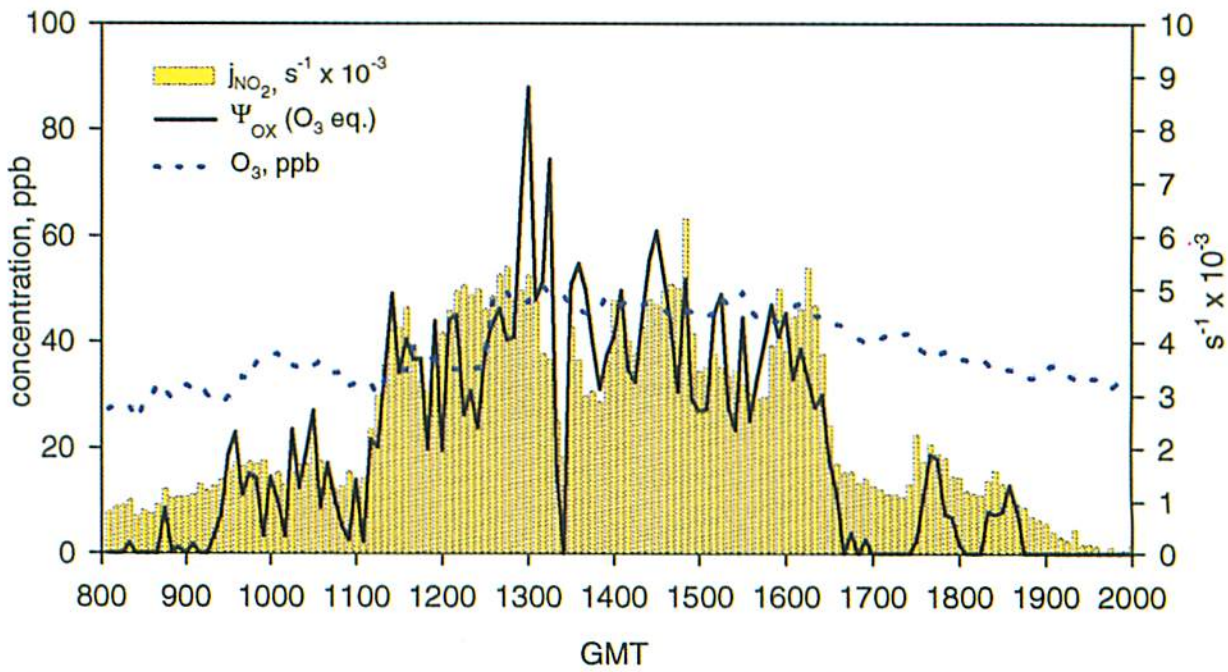

Figure 2.3 Diurnal variation of the missing oxidant (Ψ_{ox}) observed at Bush, Midlothian (18th August 1993) derived from measurements of deviations from the NO-NO_2-O_3 photostationary state, and observed concentrations of O_3 and the NO_2 photolysis rate, J_3 (see discussion in text). Data supplied by J.N. Cape, ITE, Edinburgh.

The lifetime of NO_2 with respect to this reaction in the sunlit boundary layer is typically of the order of 2 hours ($[HO_2]$ = 10 ppt; 2.5 x 10^8 molecule cm^{-3}). However, HO_2NO_2 is thermally unstable and only has a lifetime of the order of 30 seconds with respect to decomposition by the reverse reaction at 288 K and atmospheric pressure. Consequently, NO_2 is readily regenerated and the contribution of HO_2NO_2 to NO_Y is limited.

The addition reaction of OH with NO leads to the production of HONO, with the boundary layer lifetime of NO with respect to this reaction being *ca* 2 days for [OH] = 0.04 ppt (10^6 molecule cm^{-3}), and *ca* 5 hours for [OH] = 0.4 ppt (10^7 molecule cm^{-3}):

$$OH + NO\ (+M) \rightarrow HONO\ (+M) \qquad (9)$$

Once again, HONO only acts as a temporary reservoir for NO_X, since it is readily photolysed by near ultra-violet radiation, its photolysis lifetime typically being less than 1 hour (see Section 2.3):

$$HONO + \text{sunlight} \rightarrow OH + NO \qquad (10)$$

As a result, HONO is unable to accumulate significantly during daylight hours, and is often undetectable. Where daytime measurements are possible, it provides a potential tracer for OH radicals, provided its photolysis rate (J_{10}) and the concentration of NO are also measured:

$$[OH] = J_{10}[HONO]/k_9[NO] \qquad (v)$$

This relation only holds, however, if reaction (9) is the sole (or dominant) daytime source of HONO. Observational data are consistent with the existence of additional thermal sources of HONO, which may operate throughout the diurnal cycle, leading to an accumulation of HONO during the night, followed by photolysis at sunrise (e.g. Harris *et al*, 1982; Kessler and Platt, 1984; Harrison *et al*, 1996). The available information is consistent with HONO production from heterogeneous reactions involving the NO_X species and H_2O, which will be discussed further in Section 2.6 and Chapter 6. During periods of photochemical activity (ie. at elevated OH concentrations), reaction (9) is probably the major daytime source of HONO.

2.2.3 The Formation and Removal of Organic Peroxy Nitrates

The reactions of NO_2 with organic peroxy radicals (RO_2) lead to the production of compounds commonly referred to as "organic peroxy nitrates" (RO_2NO_2):

$$RO_2 + NO_2\ (+M) \leftrightarrow RO_2NO_2\ (+M) \qquad (11)$$

Conversion of NO_2 to organic peroxy nitrates by reaction (11) occurs only about an order of magnitude more slowly than photodissociation (reaction (3)). The thermal stability of peroxy nitrates is, however, strongly dependent on the structure of the organic group "R", as shown in Table 2.1. Simple alkyl peroxy derivatives, such as $CH_3O_2NO_2$, are unstable and decompose on the timescale of about 1 second under typical boundary layer conditions. Consequently, the equilibrium (11) is rapidly established, with only a very small amount of NO_X sequestered in the form of the peroxy nitrate. The presence of electron-withdrawing substituents in the organic group, however, tends to increase the thermal stability of the compounds (Lightfoot *et al*, 1992). Thus, a carbonyl (C=O) group adjacent to the peroxy radical centre has a particularly marked effect on the strength of the OO-NO_2 bond, and the resultant peroxy acyl nitrates are significantly more stable than the alkyl peroxy derivatives. The simplest example of this class of compound, peroxy acetyl nitrate or PAN ($CH_3C(O)OONO_2$), was first detected in the atmosphere nearly thirty years ago (Stevens, 1969), and subsequent field measurements have established that PAN often makes a significant contribution to total NO_Y (see Chapter 4). Furthermore, PAN is invariably more abundant than its higher homologues (e.g. see Singh *et al*, 1992; Altschuller, 1993). This is mainly because the precursor peroxy radical, $CH_3C(O)O_2$, is potentially produced from the degradation of a large number of organic compounds $\geq C_2$, whereas the abundance of potential source compounds systematically diminishes for the larger $RC(O)O_2$ radicals.

Laboratory studies have established that PAN (and other peroxy acyl nitrates) typically has a lifetime of the order of hours with respect to thermal decomposition at temperatures characteristic of the planetary boundary layer (e.g. Lightfoot *et al*, 1992; Grosjean *et al*, 1994a; 1994b). As shown in Table 2.2, however, the stability of PAN is strongly dependent on temperature, its lifetime increasing dramatically as the temperature is lowered. Consequently, under appropriate meteorological conditions, characterised by rapid vertical transport accompanied by a rapid decrease in temperature, PAN and other peroxy acyl nitrates

Table 2.1 Thermal decomposition rates (k_{-11}) and lifetimes (τ) for a series of peroxy nitrates (RO_2NO_2) at 298 K and 760 Torr[a]

$$RO_2NO_2\ (+M) \leftrightarrow RO_2 + NO_2\ (+M)$$

R	k_{-11} / s^{-1}	τ
H	0.082	12 seconds
CH_3	1.7	0.59 seconds
C_2H_5	3.4	0.29 seconds
$CH_3C(O)$	0.00046	36 minutes
$C_6H_5C(O)$	0.00031	54 minutes

a. based on data taken from the compilation of Lightfoot *et al* (1992)

Table 2.2 Thermal decomposition lifetimes (τ) of PAN as a function altitude at mid latitudes[a,b]

$$CH_3C(O)OONO_2\ (+M) \rightarrow CH_3C(O)O_2 + NO_2\ (+M)$$

approximate altitude/km	T/K	P/Torr	τ
0.0	288	760	2.6 hours
2.5	273	540	1.5 days
5.0	258	390	26 days
7.5	243	280	1.9 years
10.0	228	200	75 years

a. Based on data taken from the compilation of Lightfoot *et al* (1992); b. The increase of τ with altitude is almost entirely due to the decrease in temperature.

become stable molecules which may only be degraded to release NO_x on a much longer timescale, either by reaction with OH radicals, or by photodissociation. At higher altitudes, concentrations of PAN have been shown to exceed those of the NO_x species (Singh *et al*, 1992; 1993).

2.2.4 The Formation and Removal of Organic Nitrates

The reactions of the organic peroxy radicals (RO_2) with NO, in addition to converting NO to NO_2 as described above (reaction (6a)), also have minor channels leading to the production of organic nitrates ($RONO_2$):

$$RO_2 + NO\ (+M) \rightarrow RONO_2\ (+M) \qquad (6b)$$

The majority of information available for these reactions is for the simple "alkyl" peroxy radicals derived from the oxidation of alkanes which have been studied in some detail, and for the corresponding alkyl nitrate products (Carter and Atkinson, 1989; Roberts, 1990; Atkinson, 1990; Lightfoot *et al*, 1992). Reaction channel (6b) is extremely minor for small peroxy radicals such as CH_3O_2 (< 0.5%) and $C_2H_5O_2$ (<1.4%), but increases with radical size up to *ca* 35% of the overall reaction for the secondary $C_8H_{17}O_2$ isomers under boundary layer conditions (Carter and Atkinson, 1989; Lightfoot *et al*, 1992). Reaction (6b) has been shown to be more important for secondary alkyl peroxy radicals than it is for primary or tertiary ones. The limited information available for peroxy radicals containing oxygenated functional groups also suggests that the formation of $RONO_2$ species is less efficient than for the corresponding unsubstituted alkyl peroxy radicals (Lightfoot *et al*, 1992; Muthuramu *et al*, 1993; Eberhard *et al*, 1995; Atkinson, 1994).

A series of nine C_1-C_5 alkyl nitrates has recently been detected, both in the boundary layer over southern England, and at various altitudes at locations over the North Atlantic (Williams 1994). Although these measurements have shown the alkyl nitrates to be present at comparatively low levels in the springtime boundary layer (typically in the range 10-20 ppt for each of methyl, ethyl, 1 and 2-propyl and 2-butyl nitrate), the data also indicate that the compounds are comparatively stable under tropospheric conditions, persisting at a similar level in aged boundary layer air masses and being transported into the background troposphere. Laboratory studies have established that alkyl nitrates are insoluble in water, and do not readily transfer to the particulate phase (Roberts, 1990; Kames and Schurath, 1992), indicating that they are ultimately degraded either by reaction with OH or by photodissociation. For small alkyl nitrates, the major loss process is photodissociation, which occurs on the timescale of about 2-4 weeks (40° latitude, springtime; Roberts and Fajer, 1989). For the larger compounds, however, attack of OH on the carbon skeleton becomes important (Atkinson, 1990;1994; Roberts, 1990). Consequently, for butyl and pentyl nitrates, removal by reaction with OH is competitive with photolysis, and the tropospheric lifetimes of the compounds become progressively shorter as the size of the carbon skeleton increases $>C_5$, owing to more rapid removal by reaction with OH. Although photolysis is known to release NO_x (Roberts, 1990), there have been no product studies of the reactions of OH with alkyl nitrates. Nevertheless, the long range transport of organic nitrates, and the peroxy acyl nitrates referred to in Section 2.2.3, is believed to provide a major source of NO_x in the background troposphere (Singh *et al*, 1992).

2.3 The Role of Volatile Organic Compounds in Photochemical Ozone Formation

2.3.1 General Description

It has been established for some decades (Haagen-Smit and Fox, 1954; 1956; Leighton, 1961) that the formation of ozone (O_3) in the troposphere is promoted by the presence of volatile organic compounds (VOC; for example, hydrocarbons), NO_x and sunlight, and the mechanism by which this occurs is now well understood (Atkinson, 1990; 1994; Lightfoot *et al*, 1992). The sunlight initiates the process by providing near ultraviolet radiation which is able to dissociate certain stable molecules, leading to the formation of hydrogen-containing free radicals (HO_x). In the presence of NO_x, these free radicals catalyse the oxidation of VOCs, ultimately to carbon dioxide and water vapour. Partially oxidised organic species such as aldehydes, ketones and carbon monoxide are produced as intermediate oxidation products, with ozone formed as a by-product.

The details of the chemistry are shown schematically in Figure 2.4 for the oxidation of a generic saturated

hydrocarbon, RH (ie. an alkane), into its first generation oxidised products. In common with the tropospheric oxidation of most organic compounds, the oxidation is initiated by reaction with the hydroxyl radical (OH), leading to the following rapid sequence of reactions:

$$OH + RH \rightarrow R + H_2O \quad (12)$$
$$R + O_2 (+M) \rightarrow RO_2 (+M) \quad (13)$$
$$RO_2 + NO \rightarrow RO + NO_2 \quad (6a)$$
$$RO \rightarrow \text{carbonyl product(s)} + HO_2 \quad (14)$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad (5)$$

Since OH is regenerated, this mechanism is a catalytic cycle with OH, the alkyl radical (R), the alkyl peroxy radical (RO_2), the alkoxy radical (RO) and the hydroperoxy radical (HO_2) acting as chain propagating radicals. Reactions (5) and (6a), involving the peroxy radicals, play a key role in O_3 formation, since NO is oxidised to NO_2. As discussed in Section 2.2.1, NO_2 is efficiently photodissociated by near ultra-violet and visible radiation to generate O_3 as follows:

$$NO_2 + \text{sunlight } (\lambda < 420 \text{ nm}) \rightarrow NO + O \quad (3)$$
$$O + O_2 (+M) \rightarrow O_3 (+M) \quad (4)$$

The abbreviated reaction (14) shows that the RO radical is converted into HO_2 as part of the chain propagating process leading to the regeneration of OH. The mechanism of reaction (14) is strongly dependent on the structure of RO, and therefore on the structure of the parent organic compound. For small alkoxy radicals (e.g. CH_3O), conversion to HO_2 is achieved in a single step by reaction with O_2, also yielding an aldehyde or ketone oxidation product $R_{-H}O$ (e.g. in the case of CH_3O, the product is formaldehyde, HCHO):

$$RO + O_2 \rightarrow R_{-H}O + HO_2 \quad (14')$$

Larger or more complex RO radicals may also thermally decompose or isomerise (if they contain a carbon chain $\geq C_4$). In these cases, a sequence of reactions may occur prior to the generation of HO_2. Assuming reaction (14') is the fate of RO, the overall chemistry of the oxidation of RH into its first generation product $R_{-H}O$ (one "cycle" in Figure 2.4) is given by the following equation:

$$RH + 4O_2 \rightarrow R_{-H}O + H_2O + 2O_3 \quad (15)$$

Thus, the oxidation of one molecule of RH to $R_{-H}O$ (catalysed by HO_x and NO_x) is accompanied by the generation of two molecules of O_3. As discussed in the next section and shown in the figure, O_3 photolysis is a major source of HO_x radicals. It may therefore be regarded as an autocatalyst, since it stimulates its own production via the chemistry described above.

The further oxidation of the first generation product, $R_{-H}O$, also follows the same general pattern (ie.

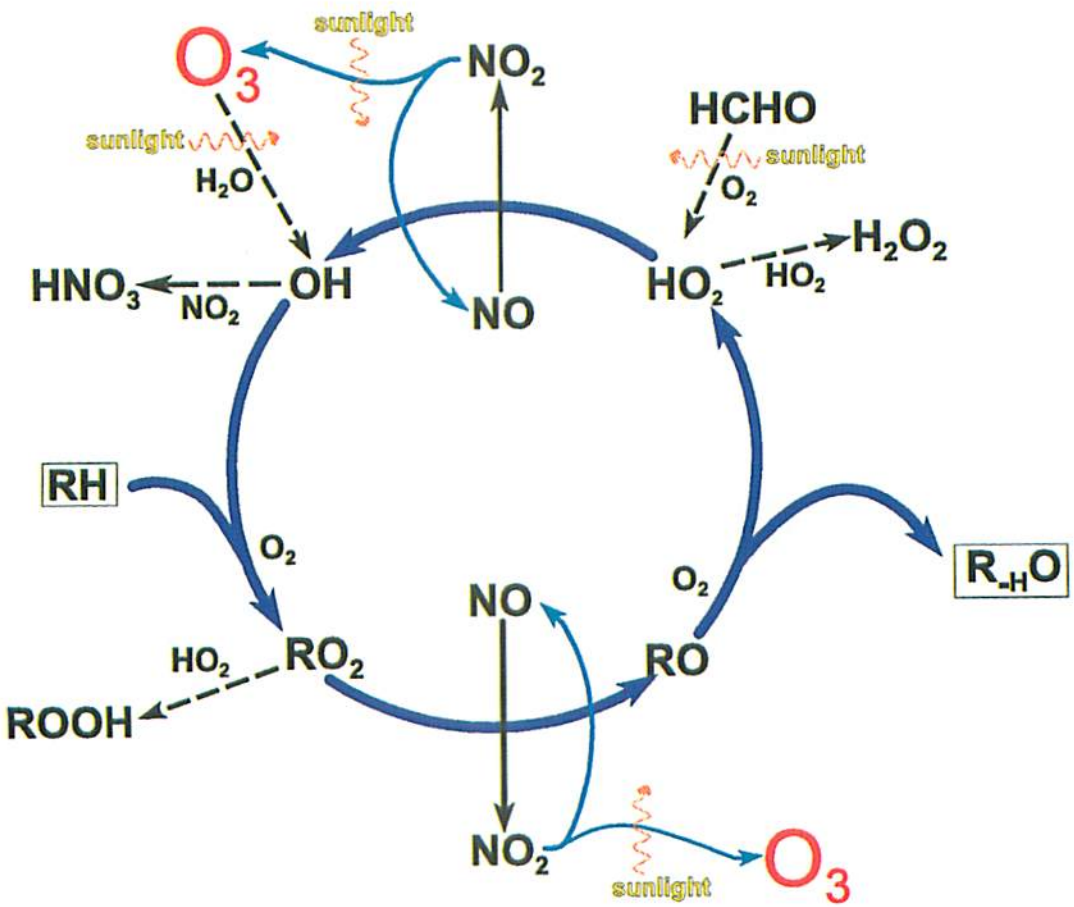

Figure 2.4 Schematic representation of the free radical-catalysed oxidation of a generic saturated hydrocarbon, RH, to its first generation oxidised product, $R_{-H}O$. The key role played by the NO_x species in the chain-propagating process is also illustrated, which leads to the generation of O_3 as a by-product. The major sources and sinks of the free radicals are also shown (detailed discussion is given in the text).

generating O_3), and subsequent organic products are, in turn, oxidised until CO_2 is eventually produced. The penultimate oxidised product is commonly carbon monoxide (CO), for which the atmospheric oxidation of organic compounds is therefore the major global source. Its oxidation to CO_2 (achieved by reaction with OH radicals) also generates HO_2, and therefore O_3 by the chemistry described above:

$$OH + CO \rightarrow H + CO_2 \quad (16)$$

$$H + O_2 (+M) \rightarrow HO_2 (+M) \quad (17)$$

In the polluted troposphere, direct emissions of CO as a result of combustion processes are often the major local source, and therefore make some contribution to O_3 production in the boundary layer.

The chemistry outlined above specifically describes the oxidation of an alkane. The OH radical initiated oxidation of other VOCs (and of the oxygenated products of alkane degradation referred to above) generally occurs by very similar mechanisms, the details of which are reasonably well understood. For many small VOCs (e.g. methane (CH_4), ethane (C_2H_6), ethene (C_2H_4), methanol (CH_3OH), t-butanol ($(CH_3)_3COH$), acetaldehyde (CH_3CHO), acetone (CH_3COCH_3) and dimethyl ether (CH_3OCH_3)), the rates and products of the elementary reactions involved in their oxidation have received a great deal of attention, and the mechanisms are very well established (see, for example, Atkinson, 1990; 1994; Jenkin *et al*, 1997). For many other VOCs, oxidation mechanisms defined by analogy are fully consistent with available experimental data, and it is also possible to predict with reasonable confidence oxidation mechanisms for some compounds for which little or no experimental data exist, by use of structure-reactivity correlations (e.g. Kwok and Atkinson, 1995; Jenkin *et al*, 1997). In view of the very large number of VOCs emitted into the atmosphere, the use of such correlations is essential in mechanism construction. There are, however, still significant uncertainties in the oxidation mechanisms of some common complex VOCs, such as aromatic hydrocarbons and terpenes, although new data are constantly emerging.

The rate of oxidation of VOCs (and therefore production of O_3) is governed by the ambient concentration of the catalytic HO_x radicals, which is controlled by a balance between production and removal routes. In the subsections which follow, the major sources and sinks of HO_x radicals are described.

2.3.2 Sources of HO_x Radicals

HO_x radicals are generated by the photodissociation of certain atmospheric trace species. A strict definition of HO_x radicals would include only OH and HO_2; for the purposes of the present discussion, organic radicals are also classed as HO_x since (as described above and shown in Figure 2.4), they are readily converted to OH and HO_2 under atmospheric conditions.

The incident sunlight which penetrates to the lower layers of the atmosphere is almost entirely at wavelengths longer than *ca* 290 nm, and potential radical precursors are therefore those species which absorb light at these wavelengths. A further requirement is that the energy of the absorbed radiation is sufficient to break the weakest bond in the molecule.

The major sources of HO_x radicals, listed in Table 2.3, are the photolysis of O_3, aldehydes and HONO. In global terms, the most important tropospheric source of free radicals results from the UV photodissociation of O_3 at wavelengths shorter than *ca* 318 nm, as follows:

$$O_3 + \text{sunlight } (\lambda < 318 \text{ nm}) \rightarrow O(^1D) + O_2 \quad (18)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (19)$$

However, since the required wavelengths are near the atmospheric "cut-off" at *ca* 290 nm, the photodissociation rate J_{18} varies strongly with the changes in the atmospheric pathlength which accompany variations in altitude, latitude and season, and other sources of free radicals may be more important under specific conditions. A further influence on the production rate of OH results from competing "quenching" reactions for the electronically excited $O(^1D)$ atom:

$$O(^1D) (+M) \rightarrow O(^3P) (+M) \quad (20)$$

$$O(^3P) + O_2 (+M) \rightarrow O_3 (+M) \quad (4)$$

Available kinetic data for reactions (19) and (20) (DeMore *et al*, 1994) suggest that the fractional conversion "f" of $O(^1D)$ into OH is given approximately by the expression

$$f = P_{H_2O}/(P_{H_2O} + 0.13P) \quad (vi)$$

where P_{H_2O} is the partial pressure of water vapour and P is the total pressure. Thus, this factor has to be taken into consideration when comparing the relative importance of photolysis reactions as free radical sources.

As shown in Table 2.3, the photolysis of HCHO (reaction (21)) makes an important contribution to free radical production at the concentrations observed in the rural UK, and dominates radical production under urban conditions, when the concentration of O_3 is suppressed by reaction with NO (reaction (2)), and the concentration of HCHO is elevated due to high local emissions or production rates from hydrocarbon oxidation (see above):

$$HCHO + \text{sunlight} \rightarrow H + HCO \quad (21)$$

$$RCHO + \text{sunlight} \rightarrow R + HCO \quad (22)$$

$$H + O_2 (+M) \rightarrow HO_2 (+M) \quad (17)$$

$$HCO + O_2 \rightarrow HO_2 + CO \quad (9)$$

Similarly, the photolysis of other aldehydes (reaction (22)) can collectively make a significant contribution to radical production, particularly in polluted regions. Clearly, the photolysis of HCHO, and to a lesser extent RCHO, plays an important role in the initiation of summertime pollution at urban locations, when O_3 concentrations are initially close to zero.

HONO is photolysed very efficiently under both summertime and wintertime conditions, and is a potentially important free radical source, despite being present at very low concentrations during daylight hours:

$$HONO + \text{sunlight} \rightarrow OH + NO \qquad (10)$$

As shown in Table 2.3, a daytime concentration of 0.1 ppb, typically observed in urban locations (Kitto and Harrison, 1992; Harrison *et al*, 1996), is sufficient for HONO photolysis to make a potentially major contribution to free radical production. However, it should be stressed that the net radical source is probably significantly less than the upper limit figures shown, since a large proportion of the observed daytime HONO is derived from the reaction of OH with NO, particularly under summertime conditions:

$$OH + NO\ (+M) \rightarrow HONO\ (+M) \qquad (9)$$

Thus, only HONO generated from alternative sources (eg. thermal heterogeneous reactions of NO_x and water vapour as described in Section 2.6) leads to net radical production upon photolysis. As discussed further in Chapter 6, this is particularly significant immediately after sunrise, when observed concentrations of HONO are generally at their highest owing to its night-time generation from thermal reactions, and accumulation in the absence of sunlight (Harris *et al*, 1982; Kessler and Platt, 1984; Kitto and Harrison, 1992; Harrison *et al*, 1996). Consequently, HONO photolysis provides a pulse of free radical production in the early morning when the photolysis rate of O_3 and aldehydes is very slow owing to the long atmospheric pathlength (Harris *et al*, 1982; Jenkin *et al*, 1988).

2.3.3 Sinks and Reservoirs for HO_x Radicals

HO_x radicals are removed from the atmosphere by a variety of termination reactions (ie. not generating radical products). The molecular products of these reactions are usually termed "reservoirs", since the possibility of HO_x regeneration through thermal decomposition or photolysis often exists. The lifetimes of reservoirs with respect to these processes are very variable, and even for a given reservoir, may be a strong function of time and location (ie. temperature, pressure, solar intensity). If a reservoir is short-lived, it has only a minor effect on HO_x (e.g. the formation and thermal decomposition of HO_2NO_2 in the boundary layer, reaction (8)). If the reservoir is comparatively stable

Table 2.3 Comparison of radical sources for various scenarios under midsummer and midwinter conditions

Reaction	photolysis rate[a] (10^{-6} s^{-1})	precursor concentration (10^9 molecule cm^{-3})	radical production rate (10^4 molecule cm^{-3} s^{-1})
midsummer			
a) rural average			
$O_3 \rightarrow O(^1D) + O_2$	11.1	750 (*ca* 30 ppb)[b]	170[c]
$HCHO \rightarrow HCO + H$	16.5	40 (*ca* 1.6 ppb)[d]	130
$RCHO \rightarrow R + HCO$	2.25[e]	20 (*ca* 0.8 ppb)[d]	9
b) rural episode			
$O_3 \rightarrow O(^1D) + O_2$	11.1	2500 (*ca* 100 ppb)[f]	570[c]
$HCHO \rightarrow HCO + H$	16.5	100 (*ca* 4 ppb)[g]	330
$RCHO \rightarrow R + HCO$	2.25[e]	40 (*ca* 1.6 ppb)[g]	18
c) urban average			
$O_3 \rightarrow O(^1D) + O_2$	11.1	50 (*ca* 6 ppb)[h]	34[c]
$HCHO \rightarrow HCO + H$	16.5	500 (*ca* 20 ppb)[i]	1700
$RCHO \rightarrow R + HCO$	2.25[e]	250 (*ca* 10 ppb)[i]	110
$HONO \rightarrow OH + NO$	1240	2.5 (*ca* 0.1 ppb)[j]	310
midwinter			
a) rural average			
$O_3 \rightarrow O(^1D) + O_2$	0.176	750 (*ca* 30 ppb)[b]	2.7[c]
$HCHO \rightarrow HCO + H$	2.51	20 (*ca* 0.8 ppb)[k]	10
$HCHO \rightarrow R + HCO$	0.188[e]	15 (*ca* 0.6 ppb)[k]	0.56
b) urban average			
$O_3 \rightarrow O(^1D) + O_2$	0.176	150 (*ca* 6 ppb)[h]	0.54[c]
$HCHO \rightarrow HCO + H$	2.51	500 (*ca* 20 ppb)[i]	130
$RCHO \rightarrow R + HCO$	0.188[e]	250 (*ca* 10 ppb)[i]	9.4
$HONO \rightarrow OH + NO$	420	2.5 (*ca* 0.1 ppb)[j]	110

a. daylight average, 50° Lat.; b. see Chapter 3; c. calculated assuming 11 Torr water vapour; d. mean of data measured at Harwell Laboratory between March 22 and September 21; e. value for acetaldehyde; f. representative value; g. peak value measured at Harwell Laboratory; h. annual mean of measurements at urban sites; i. Finlayson-Pitts and Pitts, 1986; j. Harrison *et al*, 1996; k. mean of data measured at Harwell Laboratory between September 22 and March 21.

with respect to thermal decomposition or photolysis, however, it is likely that its removal by either physical processes (e.g. dry deposition) or chemical ones (e.g. reaction with OH radicals) becomes competitive or even dominant. Since this precludes the quantitative regeneration of HO_x radicals, the formation of the reservoir represents a "sink" for HO_x radicals.

On the basis of measured rate coefficients, potentially significant tropospheric sinks for HO_x radicals (compared in Table 2.4) involve either the mutual termination of two HO_x species,

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (24)$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \quad (25)$$

$$OH + HO_2 \rightarrow H_2O + O_2 \quad (26)$$

or the removal of HO_x by reaction with the NO_x species by the following reactions:

$$OH + NO_2 (+M) \rightarrow HNO_3 (+M) \quad (7)$$

$$RO_2 + NO (+M) \rightarrow RONO_2 (+M) \quad (6b)$$

The relative importance of these reactions depends strongly on ambient conditions. Reactions (24)-(26) show a second order (quadratic) dependence on the concentration of HO_x and therefore vary greatly with time of day, location and season. Reactions (6b) and (7) involving NO_x are clearly much more important in the boundary layer over Europe than in remote tropospheric environments, owing to the higher levels of NO_x. As discussed in Section 2.2.4, the efficiency of reaction (6b) relative to the alternative channel (6a) is a strong function of the size and structure of the RO_2 radical. Consequently the importance of reaction (6b) as a radical sink is influenced by the precise composition of the peroxy radical population. The figures presented in Table 2.4 were calculated assuming reaction channel (6b) accounts for 1% of the overall reaction, which is consistent with the major contribution to the RO_2 radical population being made by small peroxy radicals such as CH_3O_2 and $C_2H_5O_2$, and oxygenated peroxy radicals such as $HOCH_2CH_2O_2$ and $CH_3C(O)O_2$.

As apparent from the figures given in Table 2.4, reaction (7) is the major radical sink for conditions appropriate to the boundary layer in the UK. This reaction totally dominates radical removal at urban levels of NO_2, and also makes the main contribution under average rural conditions. At the elevated radical concentrations consistent with a photochemical episode, however, reactions (24) and (25) compete with, or possibly dominate over, reaction (7), owing to their second order dependence on $[HO_x]$. Since these reactions are the major radical sinks, the overall removal rate of HO_x (φ) is given by the following equation, to a first approximation:

$$\varphi = k_7[OH][NO_2] + k_{24}[HO_2]^2 + k_{25}[HO_2][RO_2] \quad (vii)$$

An additional contribution to radical removal is made by reactions (6b) and (26). However, reaction (6b), involving NO_x, is generally minor in comparison with reaction (7), and the second order reaction (26) is minor in comparison with reactions (24) and (25).

In addition to being an important radical sink, the self reaction of HO_2 (reaction 24) is the major source of hydrogen peroxide (H_2O_2) in the atmosphere. Consequently, H_2O_2 is a further indicator of free-radical driven photochemical pollution, and it is routinely measured in the boundary layer over the UK (see Chapter 4).

2.3.4 Sensitivity of O_3 Formation Chemistry to Changes in NO_x and VOC Concentration

The production of O_3 from the UV irradiation of mixtures of VOCs and NO_x in air was first demonstrated in the "smog chamber" studies of Haagen-Smit and coworkers (e.g. Haagen-Smit and Fox, 1954; 1956). The peak O_3 concentrations generated from various initial concentrations of NO_x and VOCs were usually presented as an "O_3 isopleth diagram" of the form shown in Figure 2.5, in which initial mixture compositions giving rise to the same peak O_3 concentration are connected by the appropriate isopleth. Although such diagrams were originally defined by experiment, the detailed chemistry leading to O_3 formation is now well understood (as outlined above), and isopleth diagrams can be generated from modelling studies using validated chemical mechanisms. In this way, diagrams can be generated for a range of different VOCs (or VOC mixtures) and for different levels of solar intensity, and such diagrams are sometimes used to assess the effect on O_3 which would result from NO_x and VOC emissions control strategies (e.g. Dodge, 1977; National Research Council, 1991).

Table 2.4 Illustrative comparison of boundary layer radical removal rates from major sink reactions[a]

midsummer, 50°Lat		urban[b]	rural[c]	rural episode[d]
HO_x + HO_x reactions				
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(24)	42	42	4200
$RO_2 + HO_2 \rightarrow ROOH + O_2$	(25)	28	28	2800
$OH + HO_2 \rightarrow H_2O + O_2$	(26)	3.5	3.5	350
HO_x + NO_x reactions				
$OH + NO_2 (+M) \rightarrow HNO_3 (+M)$	(7)	1200	240	2400
$RO_2 + NO (+M) \rightarrow RONO_2 (+M)$	(6b)	300	25	250

a. units 10^4 molecule cm^{-3} s^{-1}, the figures given are based on the following illustrative reactant concentrations, inferred from ambient measurements and modelling studies; b. urban conditions, [OH] = 1.6 x 10^6 molecule cm^{-3}; $[HO_2]$ = 2.0 x 10^8 molecule cm^{-3}; $[RO_2]$ = 7.0 x 10^7 molecule cm^{-3}; [NO] = $[NO_2]$ = 6.3 x 10^{11} molecule cm^{-3} (*ca* 25 ppb); c. rural conditions, [OH] = 1.6 x 10^6 molecule cm^{-3}; $[HO_2]$ = 2.0 x 10^8 molecule cm^{-3}; $[RO_2]$ = 7.0 x 10^7 molecule cm^{-3}; [NO] = 5.0 x 10^{10} molecule cm^{-3} (*ca* 2 ppb) $[NO_2]$ = 1.3 x 10^{11} molecule cm^{-3} (*ca* 5 ppb); d. rural episode conditions, [OH] = 1.6 x 10^7 molecule cm^{-3}; $[HO_2]$ = 2.0 x 10^9 molecule cm^{-3}; $[RO_2]$ = 7.0 x 10^8 molecule cm^{-3}; [NO] = 5.0 x 10^{10} molecule cm^{-3} (*ca* 2 ppb) $[NO_2]$ = 1.3 x 10^{11} molecule cm^{-3} (*ca* 5 ppb).

It is clear from Figure 2.5 that the influence of changing the concentration of NO_x or VOC on the production of O_3 is strongly dependent on the ambient conditions (in particular on the relative concentrations of NO_x and VOC). In this subsection, some features of the isopleth diagram are explained in terms of the chemistry described in the preceding subsections, with the species RH as a representative VOC.

The propensity for O_3 formation in a given air mass is essentially proportional to the number of free radical-propagated cycles (in Figure 2.4) which can occur before radical removal. This is usually referred to as the chain length for O_3 formation. Thus, when considering the influence of changing the concentration of NO_x or VOC on the production of O_3, it is the effect of such a change on the *chain length* which is important. This is determined primarily by the effect the change has on the rate of the chain terminating reactions (ie. the radical sinks) compared with the competing chain propagating reactions.

Let us first consider the situation when the relative concentration $[NO_x]/[VOC]$ is high, the condition usually referred to as VOC-*limited*. As indicated in the previous subsection, the dominant chain terminating reaction under these circumstances is reaction (7). As shown in Figure 2.4, the competing chain propagating reaction is reaction (12), which leads to O_3 formation:

$$OH + RH \rightarrow R + H_2O \qquad (12)$$

$$OH + NO_2 (+M) \rightarrow HNO_3 (+M) \qquad (7)$$

Clearly, a decrease in the concentration of RH, which might result from VOC emission controls, would decrease the chain length and hence the rate of O_3 formation. In contrast, a decrease in the concentration of NO_2, which might result from NO_x emission controls, would increase the chain length and hence the rate of O_3 formation unless a simultaneous reduction in the concentration of RH occurs. Thus, under VOC-limited conditions, O_3 formation correlates positively with the ratio $[VOC]/[NO_x]$, and the O_3 isopleths tend towards lines which pass though the origin (ie. lines of constant $[VOC]/[NO_x]$) in this region of the diagram.

At high $[VOC]/[NO_x]$ ratios, or NO_x-*limited* conditions, the dominant chain-terminating reactions are (24) and (25). As discussed in the previous subsection, this circumstance is more readily achieved at higher total radical concentrations, so that the $[VOC]/[NO_x]$ ratio required for NO_x-limited conditions to prevail is also influenced by the solar intensity. As presented schematically in Figure 2.4, the ozone formation chain length under these conditions is determined by a competition between reactions (5) and (24),

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (5)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (24)$$

and between reactions (6a) and (25):

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (6a)$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (25)$$

In contrast to the VOC-limited scenario, the key chain propagating reactions (5) and (6a) involve NO_x and, consequently any reduction in NO_x decreases the O_3 formation chain length. Since RH is not itself directly involved in these competitions, the O_3 formation chain length is insensitive to changes in the level of RH which might result from VOC emission control. Thus, under NO_x-limited conditions, O_3 formation correlates positively with $[NO_x]$, and the O_3 isopleths tend towards lines which run parallel with the VOC axis (ie. lines of constant $[NO_x]$) in this region of the diagram. It should be noted, however, that variation of the concentration of some VOCs has an effect on O_3 formation under NO_x-limited conditions, resulting from an indirect influence on the ambient concentration of NO_x. This arises because the degradation of some VOCs can lead to the significant removal of NO_x as organic nitrates and peroxy nitrates (see Sections 2.2.3 and 2.2.4).

Figure 2.5 clearly demonstrates that reduction of ozone formation is best achieved by a decrease in the VOC concentration under VOC-limited conditions, and by a reduction of NO_x concentration under NO_x-limited conditions. It is apparent from the above discussion, however, that VOC-limited conditions occur when the dominant radical sink is reaction (7), and that NO_x-limited conditions occur when reactions (24) and (25) are the major sinks. As implied by the illustration in Table 2.4, the conditions in the boundary layer over the UK and continental Europe are therefore likely to be intermediate to these extremes, or varying between them for a given air mass trajectory. Consequently, a thorough appraisal of the influence of

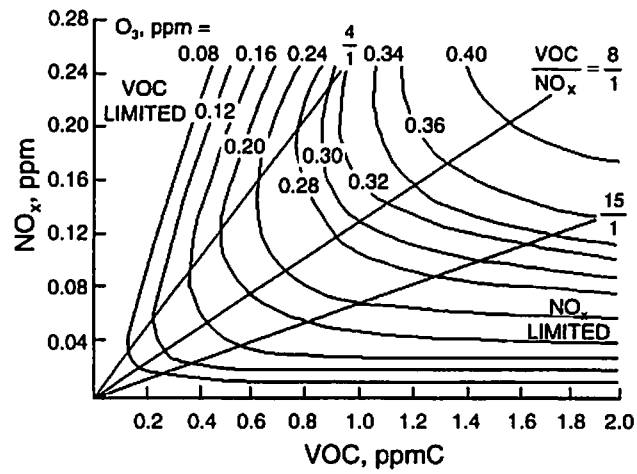

Figure 2.5 Example of an isopleth diagram illustrating calculated peak O_3 concentrations generated from various initial concentrations of NO_x and a specified VOC mixture using the US EPA empirical kinetic modelling approach (diagram adapted from Dodge, 1977). Although the methodology was originally developed for highly polluted scenarios, and the reagent concentrations on the axes are thus significantly greater than typically observed in the UK boundary layer, the characteristic shape of the O_3 isopleths as a function of VOC/NO_x ratio also applies to lower reagent concentrations (detailed discussion is given in the text).

reductions of VOC and NO_x emissions on O_3 production may best be achieved by use of suitable boundary layer trajectory models incorporating the precursor emissions and appropriate chemical mechanisms (see Chapter 9).

A further parameter of interest is the number of molecules of O_3 generated for every molecule of NO_x oxidised (e.g. to HNO_3), which may be denoted as *n*. On the basis of the above discussion, *n* would be expected to vary with ambient conditions. Under VOC-limited conditions, when the cyclic mechanism is terminated by reaction (7) (ie. converting NO_2 to HNO_3), *n* is essentially equal to the chain length (ie. the number of O_3 molecules generated by the free radical-propagated mechanism before termination occurs). Thus, as described above, the precise value of *n* depends on the VOC/NO_x ratio. Values of *n* inferred from ambient measurements (Derwent *et al*, 1994) or calculated using boundary layer models (Derwent and Davies, 1994), are consistent with values in the region of 1-10 under comparatively polluted conditions in the boundary layer over Europe. Under extreme NO_x-limited conditions, when reactions (24) and (25) are the only termination reactions, the O_3 formation mechanism does not oxidise NO_x and, in principle, *n* has an infinite value. However, the minor participation of reaction (7) under realistic NO_x-limited conditions, and the additional removal of NO_x as organic nitrates and peroxy nitrates places an upper limit on the value of *n* which may be achieved. Available calculations (e.g. Collins *et al*, 1995) suggest values as high as 100 may be possible in the remote boundary layer and the free troposphere, although it is unlikely that values greater than *ca* 30 can occur in the boundary layer over Europe.

It should be noted that the observed yield of O_3 relative to the oxidation of NO_x is also influenced by the night-time oxidation of NO_x by thermal reactions, which leads to the removal of O_3 (ie. *n* is generally negative at night). The chemistry involved is discussed further below in Section 2.4.

2.3.5 VOC Oxidation Initiated by Reaction with O_3

Unsaturated VOCs such as alkenes and dienes, in addition to reacting rapidly with OH, may also be oxidised by reaction with O_3 (Atkinson and Carter, 1984; Atkinson, 1994). The importance of reaction with OH and O_3 for a series of VOCs detected at rural locations in the UK is compared in Table 2.5. It is clear that O_3-initiated oxidation makes an important contribution, in particular for the more alkyl-substituted alkenes such as the 2-butene isomers and 2-methyl 2-butene.

Although the details of the oxidation mechanisms are less well known than for those following OH attack, the main features are well established (Atkinson, 1994). The mechanism proceeds via addition of O_3 to the double bond, leading initially to formation of an energy rich ozonide. This ozonide decomposes rapidly by two possible channels, each forming a carbonyl compound and a "Criegee" biradical which also possesses excess energy (denoted by ‡). For example, in the case of propene, this may be represented as follows:

$$O_3 + CH_2 = CHCH_3 \rightarrow HCHO + [CH_3CHOO]^{\ddagger} \quad (27a)$$

$$\rightarrow CH_3CHO + [CH_2OO]^{\ddagger} \quad (27b)$$

The energy rich Criegee biradicals are either collisionally stabilised, or decompose to yield a range of radical and molecular products. For $[CH_3CHOO]^{\ddagger}$, available information is consistent with the following being probable major reactions:

$$[CH_3CHOO]^{\ddagger} (+M) \rightarrow CH_3CHOO (+M) \quad (28)$$

$$[CH_3CHOO]^{\ddagger} \rightarrow CH_3 + CO + OH \quad (29a)$$

$$\rightarrow CH_3 + CO_2 + H \quad (29b)$$

$$\rightarrow CH_4 + CO_2 \quad (29c)$$

The predominant reaction for the stabilised biradicals (such as CH_3CHOO formed in reaction (28)) under tropospheric conditions is believed to be the reaction with water vapour, which can lead to the formation of carboxylic acids, hydroxyalkyl hydroperoxides and H_2O_2 (Atkinson, 1994 and references therein), e.g.:

$$CH_3CHOO + H_2O \rightarrow CH_3C(O)OH + H_2O \quad (30a)$$

$$\rightarrow CH_3CH(OH)OOH \quad (30b)$$

$$\rightarrow CH_3CHO + H_2O_2 \quad (30c)$$

However, they may also play a minor role in the oxidation of trace atmospheric species, for example SO_2 (Cox and Penkett, 1971; 1972):

$$CH_3CHOO + SO_2 \rightarrow CH_3CHO + SO_3 \quad (31)$$

Reactions (29a) and (29b) show that the production of free radicals from the O_3-initiated oxidation of alkenes can occur. Since free radicals catalyse the formation of O_3, as described above, it is apparent that the reactions of O_3 with alkenes do not necessarily constitute a sink for O_3. Laboratory measurements of OH radical production (eg. Atkinson and Aschmann, 1993; Atkinson, 1994) indicate that the yield increases with alkyl substitution of the double bond, for example *ca* 30%, 60% and 90% for propene, the 2-butene isomers and 2-methyl 2-butene respectively. The more substituted alkenes also tend to have an increased reactivity towards O_3 and (as shown in Table 2.5) are therefore those most likely to react with O_3 under tropospheric conditions. Consequently it is likely that the tropospheric reactions of O_3 with alkenes lead to significant radical formation and, depending on the ambient conditions, possible net O_3 production. It is also clear that these reactions can generate radicals at night, as will be discussed further in Section 2.4.3.

Table 2.5 Comparison of chemical lifetimes of selected VOCs detected at UK rural sites with respect to reaction with OH, O_3 and NO_3 at assumed ambient levels

VOC	OH[a]	O_3[a]	NO_3[a]
alkanes			
ethane	29 days		65 years
propane	6.3 days		5.6 years
butane	2.9 days		1.9 years
2-methyl propane	3.1 days		1.1 years
pentane	1.8 days		1.1 years
2-methyl butane	1.9 days		11 months
alkenes			
ethene	20 hours	9.7 days	5.2 months
propene	6.6 hours	1.5 days	3.5 days
1-butene	5.5 hours	1.6 days	2.5 days
2-butene	2.9 hours	2.4 hours	2.1 hours
2-methyl propene	3.4 hours	1.4 days	2.4 hours
1-pentene	5.5 hours	1.5 days	2.5 days[b]
2-pentene	2.6 hours	2.4 hours[b]	2.1 hours[b]
2-methyl 1-butene	2.8 hours	1.4 days[b]	2.4 hours[b]
3-methyl 1-butene	5.5 hours	1.6 days[b]	2.5 days[b]
2-methyl 2-butene	2.0 hours	55 minutes	5.1 minutes
1,3-butadiene	2.6 hours	2.4 days	7.9 hours
isoprene	1.7 hours	1.2 days	1.2 hours
aldehydes			
formaldehyde	18 hours		1.9 months
acetaldehyde	11 hours		12 days
aromatics			
benzene	5.7 days		
toluene	1.2 days		1.3 years
ethyl benzene	23 hours		
o-xylene	12 hours		2.9 months
m-xylene	7.1 hours		4.7 months
p-xylene	12 hours		2.4 months
sulpur-containing organics			
dimethyl sulphide	1.5 days		43 minutes
dimethyl disulphide	46 minutes		1.1 hours

a. concentrations used in calculations: [OH] = 1.6×10^6 molecule cm^{-3} (*ca* 0.06 ppt), [O_3] = 7.5×10^{11} molecule cm^{-3} (*ca* 30 ppb), [NO_3] = 3.5×10^8 molecule cm^{-3} (*ca* 15 ppt); b. rate coefficient estimated by analogy.

2.4 Night-Time Chemistry

Although the major oxidation processes in the troposphere are initiated by the presence of sunlight, there are potentially significant chemical processes which can occur during the night. These processes cannot generate O_3 (indeed, they lead to O_3 removal), but potentially do produce a series of secondary pollutants, including H_2O_2. The chemistry also oxidises NO_x and VOCs which, as described above, are precursors to the formation of O_3 and other secondary photochemical pollutants during daylight. In this section, current understanding of night-time chemistry is summarised, with particular emphasis placed on the role of the nitrate radical, NO_3.

2.4.1 The Formation of NO_3 and N_2O_5

Throughout the diurnal cycle, NO_2 is slowly converted into NO_3 by reaction with O_3, which occurs on the timescale of *ca* 12 hours at a typical boundary layer O_3 concentration of 30 ppb:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (32)$$

During daylight, however, NO_3 is photolysed extremely efficiently (on the timescale of a few seconds), leading mainly to the regeneration of both NO_2 and O_3,

$$NO_3 + \text{sunlight} \rightarrow NO_2 + O \qquad (33)$$

$$O + O_2 (+M) \rightarrow O_3 (+M) \qquad (4)$$

and also regenerates NO_2 by reaction with NO:

$$NO_3 + NO \rightarrow 2NO_2 \qquad (34)$$

Consequently, its importance in daytime chemistry is severely limited. At night, however, the chemistry of both NO_3 and NO_x differs from the daytime behaviour. In addition to the absence of sunlight itself, the concentrations of the free radical species OH, HO_2 and RO_2 are significantly suppressed, since they are produced mainly from the photolysis of stable molecules. Thus, once formed from reaction (2), NO_2 cannot be photolysed to regenerate NO, or removed at a significant rate by reaction with OH (reaction (7)). Provided the ambient concentration of O_3 is sufficiently high, therefore, NO is rapidly converted to NO_2 (reaction (2)), which in turn is slowly converted to NO_3 by reaction (32), as shown schematically in Figure 2.6. Reaction (34) is therefore generally unimportant at night, since NO is only present in significant concentrations close to

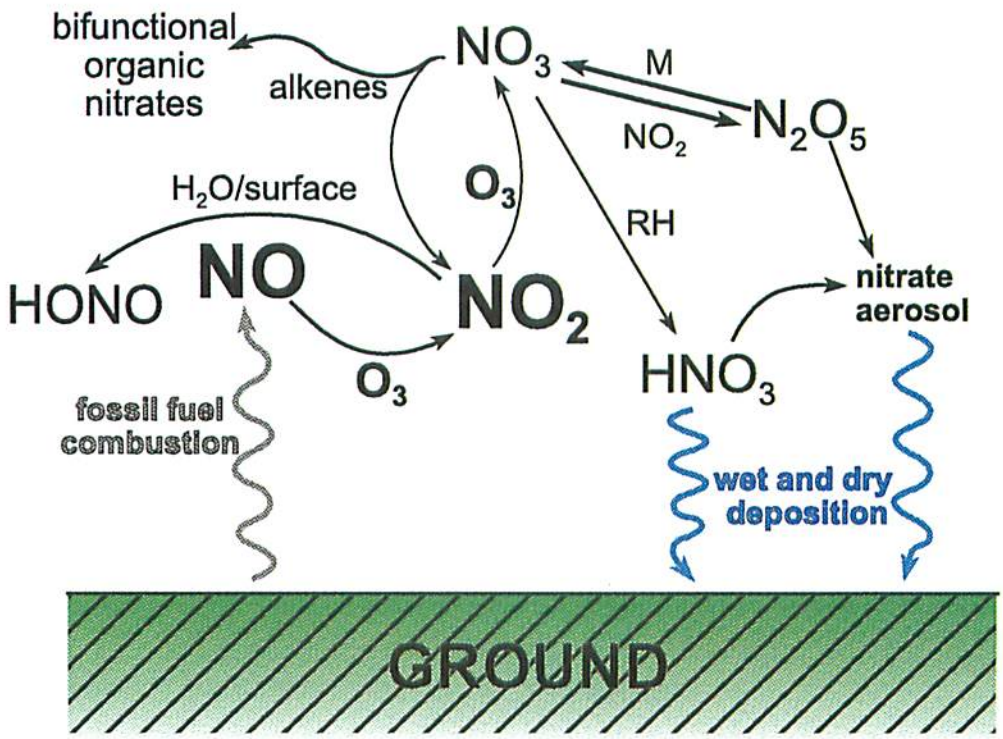

Figure 2.6 Night-time interconversions of oxidised nitrogen compounds in the troposphere.

points of emission where O_3 has been completely titrated, and NO_3 cannot be formed. The principal reaction of NO_3 at night is with NO_2:

$$NO_3 + NO_2 (+M) \leftrightarrow N_2O_5 (+M) \qquad (35)$$

The lifetime of NO_3 with respect to this reaction is about 2 seconds for an ambient [NO_2] of *ca* 10 ppb (Atkinson *et al,* 1992). However, since the product N_2O_5 is thermally unstable and decomposes on a similar timescale (*ca* 15 seconds at 298 K), the equilibrium (35) is readily established with NO_3 and N_2O_5 present in comparable concentrations. As a result, their behaviour is strongly coupled and any process removing one of the species is also a sink for the other. Thus, at sunrise both species rapidly fall to very low concentrations due to the efficient photodissociation of NO_3.

A major removal process for N_2O_5 (and therefore NO_3) at night is the reaction of N_2O_5 with water vapour:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (36)$$

Laboratory studies of this reaction have shown it to occur extremely slowly in the gas phase (Atkinson *et al,* 1992). In the troposphere it is believed to occur predominantly in cloud water and on the surface of particulate, presumably involving the "charge transfer" or "ionic" intermediate $NO_2^+NO_3^-$, with the product being nitrate aerosol rather than gaseous HNO_3 (see Section 2.6). Owing to its heterogeneous nature, the rate of this reaction is variable and difficult to define under tropospheric conditions. The timescale for removal of N_2O_5 on the tropospheric aerosol is believed to vary from the order of minutes in highly polluted air characterised by high particle densities and surface areas, to several hours in more remote, continental regions (Dentener and Crutzen, 1993).

2.4.2 The Reactions of NO_3 with Volatile Organic Compounds

The reactions of NO_3 with trace organic compounds also potentially contribute to its removal at night. The rates of removal of NO_3 by reaction with a range of alkanes, alkenes, aldehydes, aromatics and sulphur-containing organics ($\leq C_5$) at mean concentrations observed at rural sites in the UK are given in Table 2.6. From these data it is clear that the sulphur-containing organics are very significant for scavenging NO_3 at coastal locations. However, the most important class of organic compound at inland rural locations appears to be the alkenes, and in particular 2-methyl propene (i-butene) makes a significant contribution to NO_3 removal. Whereas the reactions with other organic compounds convert NO_3 to HNO_3,

$$NO_3 + RH \rightarrow HNO_3 + R \qquad (37)$$

the reactions with the alkenes occur by an addition mechanism, initiating a complex chemistry involving nitro-oxy substituted organic radicals, which can either regenerate NO_2 or produce comparatively stable bifunctional organic nitrate products (Wayne *et al,* 1991). For 2-methyl propene, the initial reaction has two channels, as follows:

$$NO_3 + CH_2 = C(CH_3)_2 (+M)$$
$$\rightarrow CH_2(ONO_2)C(CH_3)_2 (+M) \qquad (38a)$$
$$\rightarrow CH_2C(ONO_2)(CH_3)_2 (+M) \qquad (38b)$$

The subsequent reaction mechanism (shown schematically in Figure 2.7) is propagated by reactions of nitro-oxy substituted peroxy (RO_2) and oxy (RO)

radicals, and potentially leads to the production of the bifunctional organic nitrate product 2-nitro-oxy 2-methyl propanal, via the minor reaction channel (38b). As shown in Figure 2.7, this reaction sequence also yields HO_2, and is therefore potentially a night-time source of OH radicals by reactions (39) and (40), and H_2O_2 by reaction (24):

$$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2 \quad (39)$$
$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (40)$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (24)$$

However, the major reaction pathway (via channel (38a)) leads to the production of the unsubstituted carbonyl compounds formaldehyde (HCHO) and acetone ($CH_3C(O)CH_3$), and regenerates NO_2. Consequently, the NO_3-initiated oxidation of 2-methyl propene is believed to lead to significant regeneration of NO_x, but is a comparatively minor source of HO_x. Since the same is true for branched alkenes in general, which tend to be the most reactive towards NO_3 (Wayne *et al*, 1991; Atkinson, 1991), it is probable that, for the most part, the reactions of NO_3 with alkenes lead to significant regeneration of NO_x, thereby inhibiting the conversion of NO_x to nitrate aerosol or HNO_3 at night. The NO_3-initiated oxidation of the less alkyl substituted alkenes (e.g. the 2-butene isomers) should result in a greater yield of HO_x and bifunctional organic nitrate products, but is also likely to lead to substantial regeneration of NO_x.

On the basis of the data presented in Table 2.6, the mean total removal rate of NO_3 at night is *ca* 1.7 x 10^{-2} s^{-1}, corresponding to a lifetime of *ca* 1 minute. Assuming ambient concentrations of NO_2 and O_3 of 10 ppb and 30 ppb, this implies a mean rural night-time NO_3 concentration of *ca* 15 ppt. Although this is

Table 2.6 Comparison of scavenging rates of NO_3 by reactions with selected VOCs at measured rural ambient levels and by reaction with NO_2

VOC	concentration[a]	k[b]	scavenging rate[c]/10^5 s^{-1}
alkanes			
ethane	2.509	1.4×10^{-18}	0.01
propane	0.938	1.6×10^{-17}	0.04
butane	0.722	4.7×10^{-17}	0.08
2-methyl propane	0.353	8.5×10^{-17}	0.08
pentane	0.189	8.1×10^{-17}	0.04
2-methyl butane	0.405	9.9×10^{-17}	0.10
			0.35
alkenes			
ethene	1.020	2.1×10^{-16}	0.54
propene	0.202	9.5×10^{-15}	0.48
1-butene	0.041	1.3×10^{-14}	1.3
2-butene	0.047	3.7×10^{-13}	43
2-methyl propene	0.233	3.3×10^{-13}	190
1-pentene	0.022	1.3×10^{-14}	0.72
2-pentene	0.038	3.7×10^{-13}	35
2-methyl 1-butene	0.009	3.3×10^{-13}	7.4
3-methyl 1-butene	0.018	1.3×10^{-14}	0.59
1,3-butadiene	0.028	1.0×10^{-13}	7.0
isoprene	0.027	6.8×10^{-13}	46
			332
aldehydes			
formaldehyde	1.140	5.8×10^{-16}	1.7
other aldehydes	0.689	2.8×10^{-15}	4.8
			6.5
aromatics			
toluene	0.426	6.8×10^{-17}	0.07
o-xylene	0.078	3.8×10^{-16}	0.07
m & p-xylene	0.210	2.3×10^{-16}	0.12
			0.26
sulpur-containing organics			
dimethyl sulphide	0.138	1.1×10^{-12}	380
dimethyl disulphide	0.322	7.0×10^{-13}	560
			940
NO_2 ($\leftrightarrow$ N_2O_5 $\rightarrow$ aerosol)	**10**	**1.6×10^{-14} [d]**	**400**
			Total = 1.7×10^{-2} s^{-1}

a. based on measurements made at the Weybourne Atmospheric Observatory (R.A.Burgess, private communication) and the Harwell Laboratory (NILU); b. units cm^3 $molecule^{-1}$ s^{-1}; rate coefficients taken from compilations of Atkinson (1991) and Wayne *et al*, (1991); c. calculated assuming 1 ppb = 2.5×10^{10} molecule cm^{-3}; d. $k = K_{35}.k_{36}$, with $K_{35} = 4 \times 10^{-11}$ cm^3 $molecule^{-1}$ (Wayne *et al*, 1991) and $k_{36} = 4 \times 10^{-4}$ s^{-1}, a typical scavenging rate as calculated by Dentener and Crutzen (1993).

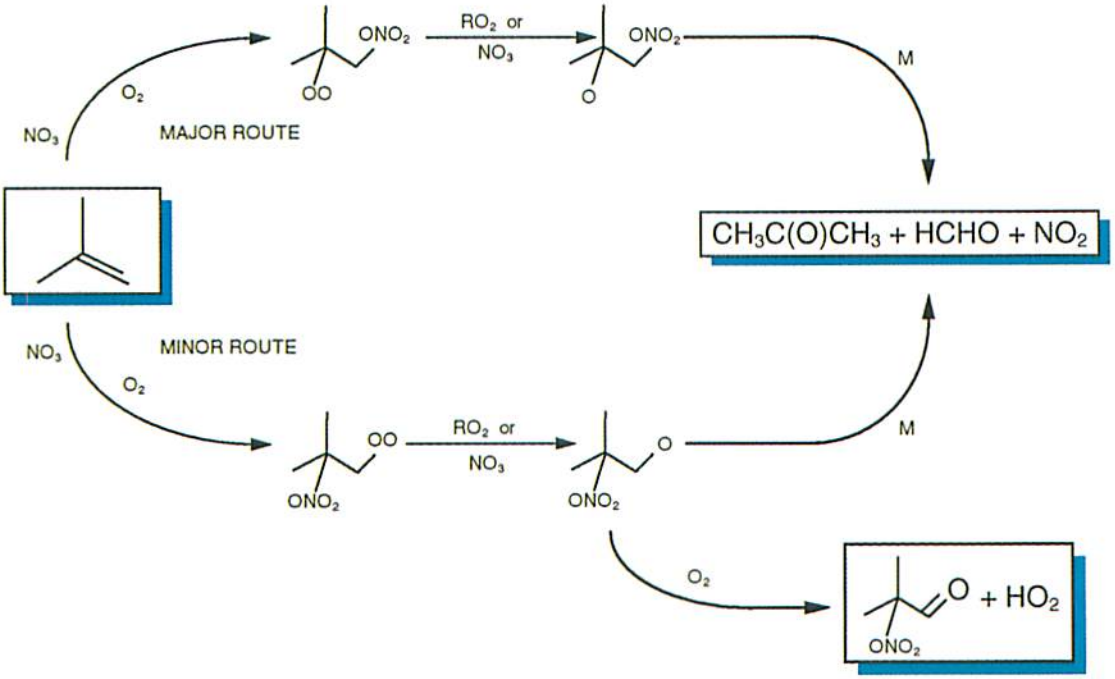

Figure 2.7 Schematic diagram of the chain propagating reactions in the NO_3 radical initiated oxidation of 2-methyl propene (*i*-butene).

consistent with the limited available UK data (e.g. see Figure 2.8), the NO_3 concentration is expected to be strongly dependent on the prevailing ambient conditions.

The above discussion has been concerned primarily with the role of the reactions of NO_3 with organic compounds in sequestering and recycling NO_X. The significance of these reactions as removal routes for the organic compounds, in comparison with removal by reactions with OH or O_3 (see Section 2.2), is also worthy of note. Using the mean night-time NO_3 concentration calculated above, the lifetimes of a series of organic compounds with respect to reaction with NO_3 can be calculated, as shown in Table 2.5. Clearly, certain compounds are potentially removed by reaction with NO_3 at a rate which is comparable with, or greater than, the rate of removal by OH and O_3, indicating that these reactions should be included in tropospheric models. However, it should be noted that NO_3 initiates, but does not catalyse, the removal of organic compounds. Consequently, its concentration can be substantially suppressed (ie. to very much lower than 15 ppt) by the presence of an organic compound with which it reacts rapidly. Under such circumstances, the lifetimes presented in Table 2.5 may be significantly underestimated.

2.4.3 Night-time Sources of HO_X Radicals

Although major sources of HO_X radicals result from photolytic processes (see Section 2.3.2), generation can also occur from a number of thermal reactions which have already been discussed in this chapter, namely the reactions of NO_3 with organic compounds (Section 2.4.2), the reaction of O_3 with alkenes (Section 2.3.5) and the thermal decomposition of peroxy acyl nitrates (Section 2.2.3). These reactions therefore potentially generate HO_X at night, and in the winter months when the photolysis processes are slow. On the basis of observed concentrations of alkenes and peroxy acyl nitrates, it is possible to estimate HO_X production rates which are as high as several percent of the rural summertime photolytic production rates presented in Table 2.3. However, current uncertainties in the radical yields from the reactions of O_3 and NO_3 with alkenes make such estimates approximate.

Significant peroxy radical concentrations have been detected at night using the chemical amplification technique (Carslaw *et al,* 1997), and these show a reasonable correlation with simultaneous measurements of NO_3 (see Figure 2.8). The sharp rise in peroxy radical concentrations from the low values observed at sunset, and the corresponding drop at sunrise

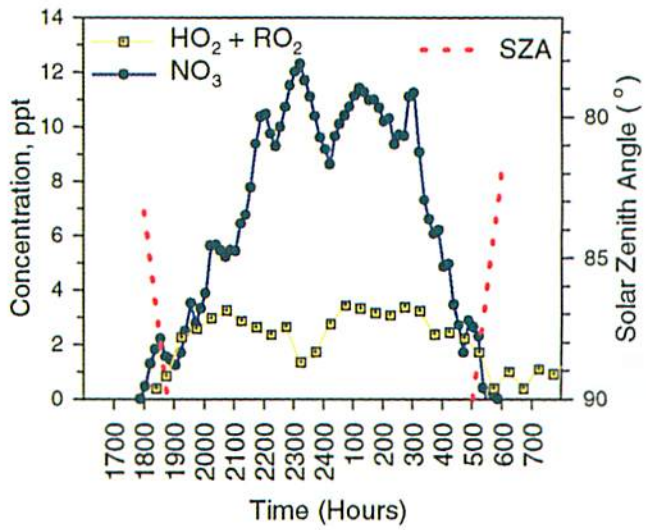

Figure 2.8 Overnight concentrations of NO_3 measured at the Weybourne Atmospheric Observatory, Norfolk (15-16th April 1994). The variation of solar zenith angle indicates the times of sunset and sunrise (data taken from Carslaw *et al,* 1997).

suggest a major role for NO_3 in the chemistry leading to measurable HO_x. This may result both from its reactions with VOCs (as described above), and from its involvement in radical propagation reactions. An example of the latter is the reactions of NO_3 with acyl peroxy radicals, which can promote the decomposition of peroxy acyl nitrates by competing with the recombination reaction of the acyl peroxy radical with NO_2, e.g., for PAN:

$$CH_3C(O)O_2NO_2 (+M) \leftrightarrow CH_3C(O)O_2 + NO_2 (+M) \quad (41)$$

$$CH_3C(O)O_2 + NO_3 \rightarrow CH_3 + CO_2 + NO_2 + O_2 \quad (42)$$

$$CH_3 + O_2 (+M) \rightarrow CH_3O_2 (+M) \quad (43)$$

Thus, the presence of NO_3 facilitates the conversion of the peroxy radical reservoir, PAN, into methyl peroxy radicals (CH_3O_2) and, subsequently, HO_2 at night.

2.5 Chemical Processes Leading to Secondary Aerosol Formation

The formation of aerosols in the atmosphere has an important influence on visibility, climate and chemical processes, and is of concern since fine particulate matter is inhalable. The reduction of visibility observed in power station plumes and during photochemical episodes is mainly due to the formation and growth of large numbers of particles or droplets, which are able to absorb and scatter radiation. Similarly, the scattering and absorption of incoming solar radiation by aerosols throughout the atmosphere has a direct effect on the Earth's radiative balance (and therefore climate), by influencing the energy reaching ground level. A further indirect effect results from the role of aerosols in cloud formation (ie. hygroscopic aerosols act as cloud condensation nuclei), since clouds reflect incoming radiation. Both these effects lead to atmospheric cooling (ie. negative radiative forcing) which offsets the warming influence of radiatively active trace gases such as CO_2 (IPCC, 1994).

Aerosols in the tropospheric boundary layer may be emitted directly, or formed in situ as a result of chemical processes. Similarly to gaseous pollutants, therefore, they are usually classified as either primary or secondary respectively. There are numerous sources within these categories, which may either be natural phenomena or as a result of anthropogenic pollution (eg. Finlayson-Pitts and Pitts, 1986; Jaenicke, 1993). The sizes (ie. aerodynamic diameters) of both primary and secondary aerosols may also vary over many orders of magnitude. The complete range of sizes which is usually of interest varies from about 2 nm (the smallest size detectable with a condensation nuclei counter, and effectively a molecular cluster) to about 10 μm. At greater diameters, aerosols are not readily inhaled, and are removed comparatively efficiently from the air by sedimentation.

Secondary aerosols are generated by gas-to-particle conversions, following the formation of condensable material from gas phase oxidation processes. Since these processes are often photochemically driven, the resultant aerosol usually falls into the category of secondary photochemical pollutant. A discussion of the chemistry leading to the formation of condensable material is therefore of relevance to the present report, and is given in this section. Both primary and secondary aerosols also participate in atmospheric chemistry, by providing surfaces and aqueous droplets for removal and reaction of gaseous species: this can have an influence on gas phase oxidation processes and can also lead to further significant changes in the composition and mass of the aerosol. Selected heterogeneous and aqueous phase reactions of significance to tropospheric oxidation chemistry are considered below, in Section 2.6.

An essential prerequisite for gas-to-particle conversions to occur is the presence of a species in the gas phase at a partial pressure in excess of its saturation vapour concentration with respect to the condensed phase (ie. condensable material).

This can be achieved by emission of hot gas mixtures into a cool environment (eg. resulting from combustion processes), with the rapidly formed particulate matter falling into the category of primary aerosol. However, the major contribution to the formation of condensable material in the troposphere results from the significant emission of comparatively volatile trace gases, which are oxidised in the gas phase to yield products of much lower volatility. The subsequently formed secondary aerosol is generated either by condensation onto existing aerosol, or by nucleation to form new particles or droplets. The division between these alternative processes is important in determining the number density of the aerosol. However, a detailed discussion of factors influencing this competition is outside the scope of the present report, and the reader is directed to alternative texts (e.g. Seinfeld, 1986) for further information. In the subsections which follow, the gas phase chemistry producing a series of tropospherically significant condensable species (sulphuric acid, organic oxygenates and ammonium nitrate) is outlined.

2.5.1 The Formation of Sulphuric Acid

The most significant condensable molecule formed in the atmosphere is sulphuric acid (H_2SO_4), which has also been long recognised as the most important from the point of view of the nucleation of new particles. The major source of H_2SO_4 is the oxidation of anthropogenically-derived SO_2, although the oxidation of biogenic reduced sulphur-containing trace gases (especially dimethyl sulphide) also makes an important global contribution. The gas phase oxidation of SO_2 occurs in competition with uptake into the aqueous phase, with physical removal occurring by both wet and dry deposition. By far the predominant gas phase reaction for SO_2 in the troposphere is the reaction with the hydroxyl radical (OH), which leads to the generation of H_2SO_4 by the following sequence of reactions, first postulated by Stockwell and Calvert (1983):

$$OH + SO_2 (+M) \rightarrow HOSO_2 (+M) \quad (44)$$

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \quad (45)$$

$$SO_3 + H_2O\ (+M) \rightarrow H_2SO_4\ (+M) \quad (46)$$

The rate of reaction (44) varies as a function of temperature and pressure (Atkinson *et al*, 1992). Under typical boundary layer conditions, the lifetime of SO_2 with respect to this reaction is of the order of 2 weeks, for a typical concentration of OH of 0.04 ppt (10^6 molecule cm^{-3}), with the subsequent reactions (45) and (46) occurring in less than a second.

A possible minor gas-phase oxidation route for SO_2 (Cox and Penkett, 1971, 1972) is reaction with stabilised Criegee biradical intermediates, for example CH_3CHOO formed from the reaction of O_3 with propene (see Section 2.2.5), which generates SO_3 (and therefore H_2SO_4) as follows:

$$CH_3CHOO + SO_2 \rightarrow CH_3CHO + SO_3 \quad (31)$$

Although it is clear that the major reaction of Criegee biradicals under tropospheric conditions is with water vapour, available rate coefficients suggest a small fraction reacts with other trace gases including SO_2 (Atkinson, 1994). This is an insignificant oxidation route for SO_2, unless the production rate (and therefore concentration) of Criegee biradicals is very high. Such conditions are only likely to be achieved when particularly reactive alkenes (eg. monoterpenes) are present at elevated concentrations.

The oxidation of reduced suphur containing gases also contributes to the formation of H_2SO_4 in the troposphere. Dimethyl sulphide (DMS, CH_3SCH_3) is an important component of the bio-geochemical sulphur cycle, and is believed to be the second most important source of sulphur in the troposphere, after SO_2 production from fossil fuel combustion. Produced by marine phytoplankton, DMS is a ubiquitous component of seawater, and readily undergoes sea-to-air exchange. Its oxidation in the atmosphere may be initiated by reaction with OH, NO_3 and the bromine oxide radical, BrO. The oxidation partially yields SO_2, and therefore gaseous H_2SO_4 as described above. However, other oxidised sulphur compounds, such as methane sulphonic acid (MSA, CH_3SO_3H) and dimethyl sulphoxide (DMSO, CH_3SOCH_3), are also produced, and there is evidence for direct generation of SO_3 which is rapidly and quantitatively converted to H_2SO_4 (reaction (46)). The lifetime of DMS with respect to oxidation to these products in the troposphere is typically of the order of 2 days. The oxidation of other reduced sulphur gases such as hydrogen sulphide (H_2S), carbonyl sulphide (OCS), carbon disulphide (CS_2), methyl mercaptan (CH_3SH) and dimethyl disulphide (CH_3SSCH_3) may also contribute to the production of gaseous H_2SO_4, although the sources and magnitude of the emissions of these species are less well defined.

2.5.2 The Formation of Ammonium Nitrate

The reaction between gas phase HNO_3 (formed mainly by photochemical processes, as described in Section 2.1) and ammonia (NH_3) leads to the formation of particulate ammonium nitrate (NH_4NO_3), as described by the following equilibrium:

$$HNO_3(g) + NH_3(g) \leftrightarrow NH_4NO_3(s,aq) \quad (47)$$

This reaction is reversible, indicating that NH_4NO_3 in the condensed phase (either as a solid or in solution) can dissociate to reform the gaseous reagents. A theoretical assessment of this reaction for pure NH_4NO_3 (Seinfeld, 1986) has allowed it to be described in terms of the equilibrium dissociation constant K_{47}, the value of which depends on both temperature and relative humidity. When the concentration product $[HNO_3(g)][NH_3(g)]$ exceeds K_{47}, particulate NH_4NO_3 is generated until $[HNO_3(g)][NH_3(g)] = K_{47}$. When $[HNO_3(g)][NH_3(g)]$ is less than K_{47}, particulate NH_4NO_3 cannot be formed, and any present evaporates to generate gaseous HNO_3 and NH_3. Available field observations are generally consistent with theoretical equilibium predictions (eg. Harrison and Pio, 1983; Hildemann *et al*, 1984). There are, however, no published studies of the kinetics of the processes involved.

The importance of reaction (47) for aerosol formation is strongly dependent on ambient conditions, since NH_3 is efficiently removed by reaction with acidic "sulphate" aerosols, and both HNO_3 and NH_3 readily transfer to the aqueous phase in clouds (see Section 2.6). Consequently, favourable conditions for NH_4NO_3 particulate generation are usually only found in polluted regions where there are also substantial emissions of NH_3, and under circumstances where acidic aerosols have already been largely neutralised by uptake of NH_3.

2.5.3 The Formation of Organic Oxygenates

The production of condensable material from the tropospheric oxidation of emitted VOCs leads to the formation of secondary organic aerosols (eg. Simoneit, 1986; Pandis *et al*, 1993; Saxena *et al*, 1995). This can occur, for example, during photochemical smog episodes (ie. driven by anthropogenic pollution), but also as a natural phenomenon resulting from the rapid oxidation of some biogenic hydrocarbons (eg. monoterpenes).

As described in Section 2.3, the gas-phase oxidation of VOCs proceeds by complex mechanisms, leading initially to the production of a variety of first generation oxidised organic products. These products are either of the same carbon number as the parent VOC, or of a lower carbon number if a fragmentation process has occurred. Those of the same carbon number are invariably less volatile than the parent VOC, since they are of higher molecular weight and contain one or more polar functional groups. Key functional groups which tend to reduce the volatility of a product are, in particular, carboxylic acid *(-C(=O)OH)*, but also aldehyde *(-C(=O)H)*, ketone *(-C(=O)-)*, alcohol *(-OH)* and nitrate *($-ONO_2$)*. The possible transfer of oxidised products to the condensed phase occurs in competition with further oxidation in the gas phase which, once again, can either generate even less volatile multi-functional products of the same carbon number, or products of lower carbon number following fragmentation steps.

For all classes of VOC, the propensity for aerosol formation increases as the size of the VOC is increased. This arises partly because the reactivity of larger

organic molecules in a given class is generally greater than that of smaller ones (ie. the rate of accumulation of oxidised products increases with the size of the VOC), and partly because the volatility of the oxidation products of larger VOCs is lower. Consequently, the oxidation of larger VOCs is more likely to generate oxidised products at partial pressures in excess of the saturation vapour pressure.

For many VOCs known to be emitted, the fractional conversion to aerosol under typical tropospheric conditions is estimated to be very low indeed (Grosjean and Seinfeld, 1989). However, it is also clear that certain classes of VOC are more likely to lead to aerosol formation by virtue of their general high reactivity and types of oxidation product formed. Of particular significance are cyclic compounds, since the products of fragmentation (ie. ring opening) processes are usually of the same carbon number as the parent compound. Furthermore, in the cases of cycloalkenes, aromatic compounds and terpenes, oxidation occurs predominantly by an "addition" mechanism, so that the first generation products contain two polar functional groups. Consequently the oxidation of these classes of compound is more likely to lead to the generation of aerosol than the oxidation of similar sized compounds in other classes. For cycloalkenes and terpenes, oxidation by reaction with O_3 is potentially very important, with the possibility of the generation of very low volatility bifunctional carboxylic acids as first generation products.

Available smog chamber studies of organic aerosol formation (eg. Wang *et al*, 1992a,b) suggest that, under ambient conditions, essentially all condensable material formed from the oxidation of various VOCs will condense on to existing aerosol, and homogeneous nucleation is unlikely to occur.

2.5.4 The Hygroscopic Properties of Secondary Aerosols

The growth of aerosols by absorption of water, and their ability to act as cloud condensation nuclei, not only has an influence on their interaction with light, but also on their role in chemical processes, as described in Section 2.6. The hygroscopic properties of the inorganic acids and salts commonly observed in tropospheric aerosols have been well studied (eg. Orr *et al*, 1958; Potukuchi and Wexler, 1995). H_2SO_4, for example, is completely miscible with water, and the quantity absorbed is proportional to the water vapour pressure. Above a critical relative humidity (known as the deliquescence point), the same is true for soluble inorganic salts such as ammonium sulphate ($(NH_4)_2SO_4$), which deliquesces at *ca* 80% relative humidity, and sodium chloride (NaCl) for which the deliquescence point is *ca* 75% relative humidity. Consequently, aerosols composed of such inorganic compounds take up water efficiently, and are good cloud condensation nuclei.

The nature of organic aerosols, or aerosols containing organic material, is also of considerable interest. A common assumption is that water absorption by aerosols is due solely to the presence of water soluble inorganic compounds. This would also suggest that the condensation of organic material on to an existing inorganic (eg. sulphate) core might inhibit its growth by absorption of water. Although this may be true for condensable hydrocarbons, the same may not be the case for organic oxygenates, since they contain both polar functional groups (which are hydrophilic), and hydrocarbon chains (which are hydrophobic). Indeed, organic compounds have a wide range of aqueous solubilities, and clearly have various possible effects on the water absorption properties of aerosols.

Recent observations of particle chemical composition and water content at urban and rural locations in the USA (Saxena *et al*, 1995), have identified interesting effects of organics on the hygroscopic properties of the particles. The rural data were consistent with an enhanced effect of the organic content on water absorption, whereas the urban data suggested an inhibiting influence. This can be explained in terms of the organic component being dominated by primary organic material (eg. emitted polycyclic aromatic hydrocarbons) in urban aerosol, but by secondary organic material in rural aerosol. The organic material in primary organic aerosol is likely to be less oxygenated, and therefore not particularly soluble in water (ie. more hydrophobic). In contrast, the secondary organic material, formed as described above, contains polar functional groups and is therefore more hydrophilic. Saxena *et al* (1995) discussed the solubility and water absorption behaviour of carboxylic acids which, as indicated above, are likely to be important components of secondary organic aerosols. Small carboxylic acids such as acetic acid ($CH_3C(=O)OH$) are very water soluble, and display hygroscopic properties similar to those of inorganic acids. Larger acids such as the multifunctional compound malic acid, $HOC(=O)CH_2C(OH)C(=O)OH$ (which is sufficiently involatile to be condensable at sub-ppb concentrations) has a finite solubility in water, and behaves similarly to the inorganic salts, deliquescing at *ca* 80% relative humidity. Consequently, it is possible, in many cases, that secondary organic aerosols might possess hygroscopic properties not too different from those of inorganic aerosols.

2.6 Chemistry in the Condensed Phase

Photochemical oxidant formation and related chemistry in the troposphere occurs primarily by homogeneous gas phase reactions (see Sections 2.2-2.4). As discussed in Section 2.5, the atmosphere contains condensed material in the form of aerosol particles and liquid cloud and rain droplets; when temperatures are low enough ice and snow particles can also form. Gaseous molecules colliding with the surface of these particles may become incorporated into the condensed phase, and heterogeneous reactions can occur at the surface of both solid and liquid particles. When the particles are liquid there is also the possibility of diffusion into the bulk liquid followed by reaction. These reactions can influence the concentrations and fate of the key species involved in tropospheric photochemistry, and the important heterogeneous processes need to be considered in any valid description of the atmospheric

chemistry of O_3 and related pollutants. Boundary layer chemistry may also be influenced by heterogeneous reactions occurring at the ground surface.

Most of the information regarding heterogeneous atmospheric reactions has come from laboratory studies of the uptake rate and chemical changes occurring when selected gaseous species are allowed to interact with surfaces, either bulk or dispersed as aerosols. Reaction rates are usually expressed in terms of the reactive (or irreversible) uptake coefficient, γ, which is defined as the fraction of the collisions of a specific trace gas per unit surface area of the aerosol which leads to reaction. Similarly, the accommodation coefficient or sticking probability, α, defines the fraction of collisions leading to unreactive (or reversible) uptake. There is now a reasonably well defined theoretical treatment of the overall rate of transport and chemical reaction between gas and condensed phases. The uptake data, together with a knowledge of the surface area of the atmospheric particles, allows the calculation of heterogeneous reaction rates.

2.6.1 Aqueous Phase Chemistry

Similarly to the gas phase chemical transformations discussed in Sections 2.2-2.4, the aqueous phase or in-cloud chemistry occurring in the troposphere is complex, consisting of a large number of coupled reactions involving molecular species and free radicals (both as neutral species and as ions), which can lead to the oxidation of a range of sulphur, nitrogen and carbon containing trace compounds. Current understanding allows a reasonable description of this chemistry (eg. Seinfeld, 1986; Warneck, 1988, 1996; HALIPP, 1996). A full description of in-cloud chemistry is outside the scope of the present report, and this section is restricted to a description of the uptake and chemical transformations of selected secondary pollutants and oxidising free radicals which have direct relevance to the gas phase oxidation chemistry described above. Several atmospheric modellers have suggested that such transformations can have a measurable impact on the gas phase photochemical cycles which produce tropospheric O_3 and other secondary pollutants (Lelieveld and Crutzen, 1990; Jonson and Isaksen, 1993; Dentener and Crutzen, 1993).

As discussed in Section 2.4, N_2O_5 and NO_3 play an important role in the night-time chemistry of oxidised nitrogen species. The reaction of N_2O_5 with water leads to hydrolysis:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (36)$$

This reaction is extremely slow in the gas phase (Atkinson *et al*, 1992), but laboratory measurements (Van Doren et al 1990, Hanson and Ravishankara, 1991) show that uptake is efficient on water droplets ($\gamma = 0.04$ at 283 K) and on sulphuric acid ($\gamma > 0.1$, 225 K). Similar values have been determined for uptake on aqueous ammonium sulphate aerosols (Mozurkewich and Calvert, 1988), and also on H_2SO_4 aerosols (Lovejoy and Hanson, 1995). It can be concluded that the heterogeneous hydrolysis of N_2O_5 is an important loss process for tropospheric NO_x. Uptake of NO_3 on water droplets may also occur, but it is believed to be much less important than hydrolysis of N_2O_5 (Dentener, 1993).

For highly soluble gases, uptake into solution without reaction is very efficient. For example, $\alpha > 0.1$ for uptake of HNO_3 (Van Doren *et al*, 1990), and $\alpha = 0.18$ for uptake of H_2O_2 (Worsnop *et al*,1989) into water droplets. Thus, HNO_3 and H_2O_2 are scavenged rapidly by clouds. In aqueous solution H_2O_2 is a strong oxidising agent, and is especially important for oxidation of S(IV) to S(VI) in the conversion of SO_2 to sulphate, for the range of pH values observed in atmospheric droplets (typically between 2 and 6).

O_3 is much less soluble in water droplets and, although uptake may initially be quite efficient ($\alpha > 0.02$, Utter *et al* 1992), the liquid rapidly becomes saturated with O_3 and no further uptake can occur, unless species are present in the liquid with which it reacts, for example bisulphite (HSO_3^-) and halide ions. It is also believed that the presence of HO_x radicals in solution can lead to O_3 removal. Recent laboratory measurements (Hanson *et al*, 1992) have shown that the uptake of HO_2 into liquid water is efficient ($\alpha > 0.05$). In solution, HO_2 ionises to form the O_2^- ion:

$$HO_2 \rightarrow H^+ + O_2^- \qquad (48)$$

This has consequences for the O_3 budget, since O_2^- reacts with O_3 in solution:

$$O_2^- + O_3 \rightarrow OH + OH^- + O_2 \qquad (49)$$

The net effect on O_3 loss is further enhanced since the scavenging of HO_2 by clouds is usually in competition with the gas phase reaction of HO_2 with NO (reaction (5)), which leads to O_3 production in the gas phase (see Sections 2.2 and 2.3). Analysis of these effects on the tropospheric ozone budget suggest that about 20% of the total free tropospheric ozone loss occurs in clouds (Dentener and Crutzen, 1993), and some observational evidence for ozone loss in clouds has been reported recently (Acker *et al*, 1995). There is little information, however, on the effect of these processes on regional photo-oxidant production.

Uptake of OH and HO_2 radicals by cloud droplets has long been recognised as a potentially important removal process. Model calculations using the measured uptake coefficient for HO_2 indicate a significant reduction of the local gas-phase steady state concentration of radicals in the cloud environment, due to removal on the droplets. This has an influence, therefore, on the free radical driven oxidant formation mechanisms described in Section 2.3.

2.6.2 Heterogeneous Reaction and Removal

While cloud droplet chemistry is the most widely recognised example of heterogeneous tropospheric chemistry, there is growing evidence that important reactions occur on or in at least some types of clear air aerosol. It has been known for some time that sea salt aerosols are depleted in Cl^- and Br^- and this has been attributed to the volatilisation of HCl and HBr as these species are displaced by stronger acids such as

HNO_3 and H_2SO_4 (Ericksson, 1959; Duce, 1969), eg:

$$HNO_3(g) + NaCl(s) \rightarrow NaNO_3(s) + HCl(g) \quad (50)$$

$$H_2SO_4(g) + NaCl(s) \rightarrow NaHSO_4(s) + HCl(g) \quad (51)$$

The kinetics of uptake of HNO_3 by salt have recently been investigated in the laboratory (Fenter *et al*, 1995). A value of $\gamma = 0.025$ was measured at 298 K, and gaseous HCl was observed as the main product.

Perhaps of even more potential importance from the point of view of oxidant chemistry, is the oxidative release of chlorine from marine aerosol through reaction of nitrogen oxides with NaCl:

$$2NO_2(g) + NaCl(s) \rightarrow NaNO_3(s) + ClNO(g) \quad (52)$$

$$N_2O_5(g) + NaCl(s) \rightarrow NaNO_3(s) + ClNO_2(g) \quad (53)$$

Both nitrosyl chloride ($ClNO_2$) and nitryl chloride (ClNO) are photolysed in the troposphere with release of Cl. Since chlorine atoms are highly reactive towards VOC, in a similar way to OH, this could therefore provide an additional tropospheric oxidation pathway, with a potentially significant effect on the atmospheric lifetimes of VOC and hence on photo-oxidant formation in the marine environment. Although observations of the time dependence and relative surface concentrations of C_2-C_6 hydrocarbons have provided indirect evidence for the formation of Cl atoms in the Arctic boundary layer (Jobson *et al*, 1994), quantitative data on the heterogeneous reactions involved are needed so that the full significance of such processes can be established. N_2O_5 can also react with any water adsorbed on solid aerosols to form HNO_3 (reaction (36)).

An important process of widely accepted significance for photo-oxidant formation is the production of HONO from heterogeneous reactions between NO_x and water (see Section 2.3 and Chapter 6), for which the following have been postulated:

$$2NO_2(g) + H_2O(ads) \rightarrow HNO_3(ads) + HONO(g) \quad (54)$$

$$NO(g) + NO_2(g) + H_2O(ads) \rightarrow 2HONO(g) \quad (55)$$

There have been numerous laboratory kinetic investigations of these reactions (England and Corcoran, 1974; Sakamaki *et al*, 1983; Pitts *et al*, 1984; Svensson et al, 1987; Jenkin *et al*, 1988). These studies indicate that reaction (54) is more important than reaction (55), but that the measured rates are too slow to explain the HONO concentrations observed in the atmosphere (Jenkin *et al*, 1988). Atmospheric observations are also mainly consistent with HONO formation by reaction (54) on land or aerosol surfaces. Kessler and Platt (1984) derived a conversion rate of NO_2 to HONO of *ca* 0.6% hr^{-1} in the urban boundary layer, from night-time measurements in Jülich, Germany. Recently, Kitto and Harrison (1994) have confirmed that there is a surface source of nitrous acid by reaction of NO_2, and Harrison *et al* (1996) have derived an effective rate coefficient of $5.6 \times 10^{-6} \times 100/h\ s^{-1}$ (where h is the mixing height in m) for reaction (54) in the suburban boundary layer. Model calculations (Harris *et al*, 1982; Jenkin *et al*, 1988) have shown that HONO generated at night can give rise to substantial enhancement of early morning OH radical production, following photolysis of HONO. This leads to enhanced ozone generation, which persists throughout the day.

NH_3 is the most abundant alkaline gas emitted in to the troposphere, and its uptake by cloud droplets and acidic aerosols plays a major role in determining the rates of reactions in the condensed phase, and the partitioning of equilibria. Modelling calculations suggest that its reactive removal on sulphate aerosol is the major atmospheric sink for emitted NH_3 under most conditions (eg. Dentener and Crutzen, 1994). There are, however, comparatively few laboratory measurements of surface reaction probabilities (γ) for NH_3. The data of Huntzicker *et al* (1980) imply very high values (0.2-0.7) on H_2SO_4. However, γ is likely to be very dependent on the acidity of the aerosol, and effectively zero, once the aerosol is fully neutralised by uptake of NH_3 (ie. when the aerosol has the composition $(NH_4)_2SO_4$). This is also in accord with available field measurements (Erisman *et al*, 1988; Harrison and Kitto, 1992), from which values of γ as low as *ca* 0.002-0.007 have been inferred for almost completely neutralised aerosols. Since the aerosol composition might be regarded as $(NH_4)_{2x}H_{2-2x}SO_4$ with x varying between 0 and 1, γ could be defined in relation to x. However, Dentener and Crutzen (1994) preferred to use a single compromise value of $\gamma = 0.05$, independent of aerosol composition in global calculations, as this led to calculated NH_3 first order removal coefficients which were consistent with those inferred from field observations.

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3. MEASUREMENT NETWORKS AND AMBIENT OZONE CONCENTRATIONS IN THE UK

- The UK has a rural network of 17 stations and an urban network of 36 (1/5/97) stations which provide the broad regional spatial patterns in ozone concentrations throughout the country and the concentrations in representative urban areas respectively. The data are freely available to the public and distributed by CEEFAX/ TELE-TEXT, a freephone number and the INTERNET (details in Table 3.2 and Appendix 2).
- The annual mean ozone concentrations in the UK vary between regions and with topography. The largest mean concentrations occur in rural areas, and in all areas mean concentration increases with altitude. The low altitude (< 200 m) concentrations are largest along the south coast of England.
- Annual mean ozone concentrations are generally lower in urban areas, by on average 20% to 40% of the nearby rural concentration, representing a 5 to 10 ppb reduction.
- Ozone concentrations are, on average, larger at the coast by about 20%, the effect being restricted to the area within 5 to 10 km of the coast.
- There are clear annual and diurnal cycles in ozone concentration in the UK (and elsewhere in Europe) with a spring maximum and an autumn minimum and mid afternoon peak and nocturnal minimum respectively.
- Concentrations of ozone exceed thresholds for effects on vegetation and human health throughout the UK. The largest and most frequent exceedances occur in southern England and especially in rural areas of SE England.
- Maps of mean ozone concentrations and the thresholds for effects on vegetation and human health have been constructed for the UK. The maps are subject to considerable uncertainties as a consequence of the limited number of monitoring stations and the complexity of the landscape.
- These maps show exceedance of critical levels for effects on vegetation over large areas of the UK (detailed in the summary of effects in Chapter 7.1 and in Section 3.4).
- Maps of the average exceedance of the EPAQS ozone standard (8 hour running mean over 50 ppb) from 1990 to 1995 show exceedance of the 97th percentile threshold throughout approximately 98% of the UK.
- Trends in annual mean ozone concentration are significantly positive (at the 5% level) at 9 sites. At sites which are appreciably influenced by local pollutant sources, the trend is negative but small and variable, averaging -0.1% per year.
- The magnitude of peak concentrations has declined, with the average monthly peak concentration during the period 1986 to 1995 being 20 ppb to 30 ppb smaller than during the period 1972 to 1985 and the monthly 95th percentile showed a decline averaging 0.8 ppb per year. This is a very important improvement in air quality in the UK as the peak concentrations are associated with human health and vegetation effects.
- The exceptionally hot sunny summer of 1995 led to an expectation of peak ozone concentrations similar in magnitude to those recorded during the similarly hot sunny summer of 1976. However, although concentrations were higher than those recorded in recent years, they failed to reach the levels observed in 1976. This was partly due to reductions in emissions of precursor species in some European countries but also to air circulation patterns over Europe and the UK, which frequently brought relatively clean air into the UK from N. Europe.
- The main sink for ozone in the UK is dry deposition to the ground, which over the year represents a total of *ca* 1500 kt ozone over the country.
- In urban areas, the removal of ozone by reaction with NO represents a further sink for ozone. The depletion of ozone in the UK is greater on average than the photochemical production, so that at the downwind coast, the concentrations are generally smaller than those upwind. On a larger scale the photochemical production of ozone and other oxidants in the UK 'plume' downwind of the coast extends over several hundreds of km.
- Peak concentrations of ozone are positively associated with other pollutants such that during periods with concentrations of ozone in excess of 60 ppb, the concentrations of SO_2 and NO_2 are also substantially larger than their mean values.

3.1 Introduction

Ozone is a natural component of the atmosphere where it is formed by chemical processes. There are no significant anthropogenic or natural emissions of ozone to the air. The largest concentrations, and the bulk of the ozone mass, is present in the stratosphere where it is formed by recombination of atomic and molecular oxygen:

$$O + O_2 + M = O_3 + M$$

where M can be any molecule such as nitrogen or oxygen. Within the stratosphere the atomic oxygen is provided by the photolysis of molecular oxygen by solar UV radiation with wavelengths shorter than 280 nm. The chemistry and dynamics of stratospheric ozone are outside the remit of this review group, and the reader is directed to SORG (1996) for further information on this subject. There is, however, a transfer of stratospheric ozone to the troposphere and the contribution of stratospheric ozone to ground level concentrations has been the subject of considerable controversy in recent years (Davies and Schuepbach, 1994).

It is now widely accepted that the majority of ground level ozone is formed by photochemical processes within the troposphere rather than transport from the stratosphere. Relative to most other reactive pollutants, ozone concentrations are large throughout the country with annual mean concentrations in the range 20 to 30 ppb (parts per billion, 10^9 by volume), equivalent to 40 to 60 μg O_3 m^{-3} air at the surface (10°C and 1010 mbar), and episodes during which concentrations exceed thresholds for negative effects on vegetation and humans occur on 10 to 50 days each year throughout the country.

The reactive nature of ozone with other atmospheric gases and with natural surfaces, together with photochemical production within the boundary layer lead to large temporal and spatial variations in ambient concentration. The primary objective of this chapter is to present the ozone concentration data for the UK, with emphasis on the temporal and spatial patterns of ozone exposure and the degree to which these can be explained. The knowledge of processes which regulate ozone concentration is then taken a step further to provide detailed maps of ozone exposure for the UK which are used in subsequent chapters to assess the effects on vegetation, materials and on human health.

3.2 The National O_3 Monitoring Networks

Ambient ozone has been monitored at *ca* 70 stations throughout the UK at some time since 1972. The data from a large number of sites, urban and rural, and operated by a range of organizations have been compiled within a database (the PORG database) which contains hourly mean concentrations for all sites and site years. The PORG data are freely available on request. The locations, period of measurements and site operators are listed in Appendix 2 and the geographical locations of the sites currently operating are illustrated in Figure 3.1. Many of the early measurement stations were short term research study sites and it was not until 1986 that a rural network of ozone monitoring stations was established with 16 sites. Almost a decade of measurement data are now available from the network to define the broad features of ozone climatology throughout the country. Current data from all monitoring stations both rural and urban are available to the public on a freephone number, through CEEFAX/TELETEXT and on the internet. The information to access these data is provided in Table 3.2 and Appendix 2.

3.2.1 Operation of the National Rural Ozone Network

The network of rural sites, currently 16 (August 1996), is operated on behalf of the Department of the Environment, Transport and the Regions (DETR) by a group of organisations, each with a specific role. The arrangement makes effective use of the differing areas of expertise held by the different organisations, and allows greater independence in the assessment of the data than would be possible if only a single organisation were involved. Two key positions, a Central Management and Coordinating Unit (CMCU) and an independent Quality Assurance and Quality Control (QA/QC) Unit, were appointed for the three year period starting on 1 January 1995. The National Environmental Technology Centre (NETCEN) at AEA Technology acts as CMCU, which is responsible for the day-to-day operation of the network. The CMCU receives data by telemetry from each site, monitors output and diagnostic data for signs of system malfunctions, and passes on real-time ozone information to the Data Dissemination Unit (DDU), also at NETCEN. The DDU presents the information rapidly to the public, for example by CEEFAX/TELETEXT and the Internet.

The other key position, of QA/QC Unit for the network, is held by the National Physical Laboratory (NPL) who are responsible for maximising the accuracy and comparability of the data, and for producing the data sets in their final published form. This work involves visiting each site at least four times a year to carry out detailed calibrations and to audit site practices.

Each site has an appointed Local Site Operator (LSO), who visits the site on at least a monthly basis to carry out routine instrument maintenance and checks, and who will be called out at other times by the CMSU when the need arises.

The Equipment Support Unit (ESU) is responsible for the six-monthly servicing of the instruments, and for repairing or replacing instruments when necessary.

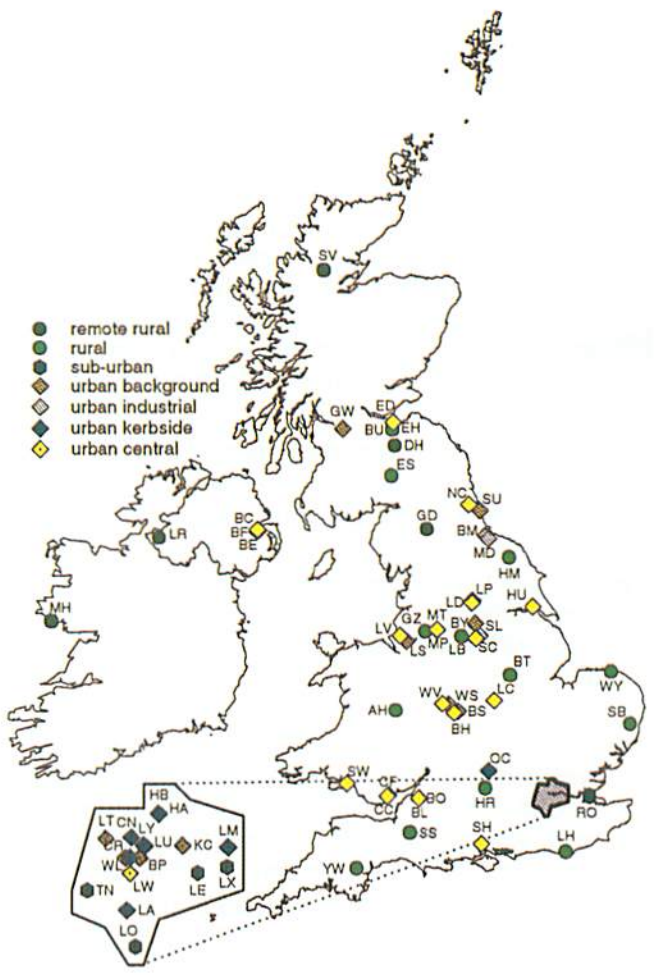


Figure 3.1 Air quality monitoring sites in the UK, 1/7/96.

Quality assurance of the data

The mechanisms for maximising the quality of the data and the level of data capture have essentially been established for several years, but are still being refined. The two main areas for assuring quality are in monitoring the performance of the measuring systems and reviewing the data before final publication.

Instrument calibration and maintenance
The instruments and associated systems are checked regularly in a number of different ways. There are daily automatic calibration checks on the analysers which are monitored by the CMSU. Every month a more thorough check is made and reported by the LSO. This work is carried out in accordance with a detailed manual written by the QA/QC Unit.

The analysers are serviced every six months by the ESU. Before and after each service, the QA/QC Unit visits every site in the network with a primary standard photometer, against which each analyser is compared, using a common ozone generator. This photometer is regularly compared with other national standards and the international standard operated by the EU Joint Research Centre at Ispra. These intercalibrations are the major mechanism by which measurement precision and accuracy throughout the network are maintained. The primary photometer is also regularly compared with the standard photometer used in the UK's urban network, to ensure consistency between both networks.

Data inspection and review
The data disseminated rapidly via the DDU has a provisional zero offset applied, and is checked for anomalous data points both by automatic algorithms and manually. However, an accurate estimate of the zero offset, and the overall behaviour of the instruments' output reading as a function of ozone concentration at any particular time, requires information from the subsequent intercalibration. The intercalibration cycle is such that a full review of the data is carried out every six months by the QA/QC Unit. At this time, information from the automatic calibrations, the LSO visits, service records, intercalibrations, and any other relevant sources are examined. Zero adjustments and scaling factors are applied to the data, wherever this is appropriate.

Where circumstances are such that there are significant uncertainties associated with certain ozone concentration data, these data are rejected. Before the provisionally ratified data is published, it is scrutinised along with the ancillary information by a quality circle including the senior project staff of the QA/QC Unit.

Precision and accuracy of the data
As the conversion of the analysers' output to an ozone reading requires both a zero offset and a scaling factor, it is appropriate to describe the uncertainty of the data with both relative and absolute values. The working estimates for these are that the data are accurate to ± 5%, with an associated precision of ± 2 ppb.

It is clear that, in practice, the uncertainty associated with a set of measurements will depend on many factors such as the condition of the particular analyser involved, and the criteria used for correcting data during data review. The assignment of measurement uncertainty of the results is currently being reviewed by the QA/QC Unit.

Data capture
The average data capture level over all ozone sites, defined as the number of ratified hourly values divided by the maximum possible number of hourly values within the year 1994, was 94.6%. This narrowly fails to meet the target of 95% data capture level set by the Department of the Environment, Transport and the Regions, though it well exceeds the reporting requirements of the EC Directive on Ozone (92/72/EEC), which specifies a 75% data capture level, distributed uniformly throughout the annual period. Five of the 16 sites had individual capture rates of less than 95%.

3.2.2 Ozone Measurements in Urban Locations Throughout the UK

Ozone is routinely measured at a number of city centre locations in the Automatic Urban Network (AUN), funded by the Department of the Environment, Transport and the Regions, see Figure 3.1 and Table 3.1 (and Appendix 2). These measurements form part of the data analysed by the Quality of Urban Air Review Group (QUARG).

This network commenced operation in 1992, at six city locations throughout the UK, and has continuously expanded since then. It is expected that the network will incorporate some 80 sites either wholly or partially funded by DETR by the end of 1997. Network operations are arranged in a manner similar to that used in the Rural network. The CMCU (Central Management and Control Unit) for sites outside London is presently TBV Science and the majority of sites within London are managed by SEIPH (the South East Institute of Public Health). Under contract to the CMCUs are the local site operators (LSOs), generally the relevant local authority in each case, and the Equipment Support Unit (ESU). The QA/QC duties are carried out by AEAT NETCEN.

Wholly DETR funded sites, as the name implies, are those for which DETR has bought the monitoring instrumentation and infrastructure, as well as paying for routine running costs through its contractors, the CMCU and QA/QC Units. Affiliated sites are those at which the instrumentation was not purchased by DETR, but the Department pays its contractors for data collection and all facets of data quality assurance and quality control. For a site to become affiliated, there are certain conditions to be met, for example relating to site location and choice of instrumentation. Manuals and training on how to carry out routine calibrations are provided for the LSOs.

The range of measurements carried out at AUN sites is greater than at rural network monitoring sites. For instance, all wholly DETR funded sites are equipped to measure O_3, NO_x, SO_2, pm10 and CO, with the majority of affiliated sites also measuring these parameters, see Table 3.1.

Table 3.1 Air quality monitoring in the UK (1\/5/97)

Site Ref	Full Name	Class	OS Grid Ref	Network/ Operator	Measurement Started	O_3	NO_x	CO	SO_2	pm10	HC
AH	Aston Hill	R	SO298901	ARN	26/06/86	X					
BC	Belfast Centre	UC	IJ339744	AUN	08/03/92	X	X	X	X	X	
BE	Belfast East	UB	IJ357740	AUN	06/09/89				X		
BF	Belfast South	UB	IJ333726	HCN	23/08/93						X
BH	Birmingham Centre	UC	SP064868	AUN	18/03/92	X	X	X	X	X	X
BL	Bristol East	UB	ST599729	HCN	01/04/94						X
BM	Billingham	UI	NZ470237	AUN	01/01/87		X				
BO	Bristol Centre	UC	ST594732	AUN	04/01/93	X	X	X	X	X	
BP	Bridge Place	UB	TQ289788	AUN	03/07/90	X	X	X	X		
BS	Birmingham East	UB	SP116889	AUN/HCN	23/08/93	X	X	X	X	X	X
BT	Bottesford	R	SK797376	ARN	01/10/77	X					
BU	Bush	R	NT245635	ARN/ITE	01/04/86	X	◊		◊		
BY	Barnsley 12	UB	SE342067	AUN	21/03/94				X		
CC	Cardiff Centre	UC	ST184765	AUN	12/05/92	X	X	X	X	X	
CF	Cardiff East	UB	ST193773	HCN	01/11/93						X
CN	London Camden	UK	TQ267843	AUN	16/05/96		X			X	
CR	Cromwell Road	UK	TQ264789	AUN	22/02/73	X	X	X	X		
DH	Dunslair Heights	RR	NT280430	ITE	1992	◊					
ED	Edinburgh Centre	UC	NT254738	AUN	04/10/92	X	X	X	X	X	
EH	Edinburgh Med. Sc.	UB	NT257730	HCN	27/08/93						X
ES	Eskdalemuir	R	NT235028	ARN	23/04/86	X					
GD	Great Dun Fell	RR	NY711322	ARN	09/05/86	X					
GW	Glasgow	UB	NS595653	AUN	06/01/87		X	X			
GZ	Glazebury	R	SJ690959	ARN	01/04/88	X					
HA	London, Haringey 1	UK	TQ339906	AUN	16/05/96		X			X	
HB	London, Haringey 2	UC	TQ339907	AUN	16/05/96	X					
HM	High Muffles	R	SE776939	ARN	16/07/87	X					
HR	Harwell	R	SU474863	ARN//HCN	22/06/76	X	X		X		X
HU	Hull Centre	UC	TA097288	AUN	04/01/94	X	X	X	X	X	
KC	Kensington & Chelsea	UB	TQ401821	AUN	01/04/96	X	X	X	X	X	
LA	London, Sutton 1	UK	TQ256646	AUN	01/04/96		X	X	X	X	
LB	Ladybower	R	SK164892	ARN	15/07/88	X	X		X		
LC	Leicester Centre	UC	SK587040	AUN	04/01/94	X	X	X	X	X	
LD	Leeds Centre	UC	SE299343	AUN	04/01/93	X	X	X	X	X	
LE	London Eltham	SU	TQ440747	AUN/HCN	04/03/93	X	X		X	X	X
LH	Lullington Heath	R	TQ538016	ARN	04/10/86	X	X		X		
LM	Tower Hamlets 2	UK	TQ521816	AUN	01/04/96		X	X			
LO	London, Sutton 3	SU	TQ278548	AUN	01/04/96	X	X				
LP	Leeds Potternewton	UB	SE307367	HCN	13/01/95						X
LR	Lough Navar	RR	IH065545	ARN	02/04/87	X					X
LS	Liverpool Speke	UB	SJ438835	HCN	01/12/95						X
LT	London Brent	UB	TQ200840	AUN	26/01/96	X	X	X	X	X	
LU	London UCL (Bloomsbury)	UK	TQ299822	HCN	11/02/93						X
LV	Liverpool Centre	UC	SJ349908	AUN	23/04/93	X	X	X	X	X	
LW	Wandsworth 2	UC	TQ264746	AUN	01/04/96	X	X				
LX	London Bexley	SU	TQ518763	AUN	01/05/94	X	X	X	X	X	
LY	London Bloomsbury	UC	TQ302820	AUN	23/01/92	X	X	X	X	X	
MD	Middlesbrough	UI	NZ505194	AUN/HCN	01/01/93	X	X	X	X	X	X
MH	Mace Head	RR	IL740320	UBRIS	1987	X					
MP	Manchester Piccadilly	UC	SJ843983	AUN	18/12/95	X	X	X	X	X	
MT	Manchester Town Hall	UB	SJ838980	AUN	22/01/87		X	X			
NC	Newcastle Centre	UC	NZ251649	AUN	08/03/92	X	X	X	X	X	
OC	Oxford Centre	UK	SP514092	AUN	15/04/96		X	X	X		
RO	Rochester	R	TQ831762	ARN	26/01/96	X	X		X	X	
SB	Sibton	R	TM364719	ARN	01/07/73	X	X				
SC	Sheffield Centre	UC	SK352869	AUN	01/01/96	X	X	X	X	X	
SH	Southampton Centre	UC	SU429121	AUN	04/01/94	X	X	X	X	X	X
SL	Sheffield Tinsley	UI	SK402906	AUN/HCN	28/11/90		X	X			
SS	Somerton	R	ST486268	ARN	26/01/96	X					
SU	Sunderland	UB	NZ398570	AUN	06/10/92				X		
SV	Strath Vaich	RR	NH347750	ARN	18/03/87	X	X		X		
SW	Swansea	UC	SS655931	AUN	01/12/94	X	X	X	X	X	
TN	Teddington	SU	TQ150700	ARN	1996	X	X		X		
WL	West London	UB	TQ251788	AUN	01/01/87		X	X			
WS	Walsall	UB	SO994982	AUN	05/03/87		X				
WV	Wolverhampton Centre	UC	SO914989	AUN	18/12/95	X	X	X	X	X	
WY	Weybourne	R	TG110430	UEA	October 1993	◊	◊	◊			
YW	Yarner Wood	R	SX786789	ARN	26/06/87	X					

ARN = Automatic Rural Network
AUN = Automatic Urban Network
HCN = Hydro-Carbon Network
UBRIS = University of Bristol, Dept. of Biogeochemistry
X = species measured
◊ = species measured continuously but not as part of a national network
UEA = University of East Anglia
ITE = The Institute of Terrestrial Ecology
RR = remote rural
R = rural
UI = urban industrial
SU = sub-urban
UK = kerbside
UC = urban central
UB = urban background

Table 3.2 Details of air quality information sources

Air Quality Monitoring Information Over the Phone

The Department of the Environment, Transport and the Regions has a freephone number for hourly updated recorded bulletins:

0800 55 66 77

Air Quality Monitoring Data and Information on the World Wide Web

The home page for all the UK air quality monitoring information can be found at WWW address:

http://www.aeat.co.uk/products/centres/netcen/airqual/welcome.html

From here several pages can be accessed :

Air Quality Bulletins	Acid Deposition Information
Air Quality Monitoring Networks	National Atmospheric Emissions Inventory
Air Quality Forecasting	Chemistry of Atmospheric Pollutants

Archive data can be viewed and downloaded from WWW pages:

http://www.aeat.co.uk/products/centres/netcen/aqarchive/archome.html

Air Quality Monitoring Data and Information on Ceefax and Teletext

Title	Ceefax page	Teletext page
Air Quality Information (main index)	**410**	**106**
General UK Forecast	411	
Wales, Scotland and Northern Ireland	412	
North England	413	
Central England	414	
South England	415	

Ozone measurements are made at the majority of AUN sites. The monitoring and calibration techniques used are similar to those used in the rural network. The instruments are UV absorption analysers and they are calibrated by on-site comparison with a UV photometer every six months, both before and after analyser service. Daily automatic checks on the analysers are also carried out.

3.2.3 Intercomparison Between Standards Used in the Rural and Urban Networks

The standard ozone photometers for both the Rural and Urban networks are retained by the relevant network QA/QC units (NPL and AEAT NETCEN respectively). Regular (six-monthly) ozone intercalibrations have been carried out between the two ozone standards since February 1995. The results of these have shown that the AEAT standard under-reads compared to the NPL standard by 2-3%.

3.2.4 European Inter-calibration Exercises

In October 1994 NPL and NETCEN visited JRC Ispra to take part in an intercomparison under the Harmonisation Directive 92/72/EEC on air pollution by Ozone. Other participants were RIVM from Holland, UBA from Germany, INERIS from France, Government standards laboratories in Spain and Italy, the Finnish Meteorological Institute and JRC at Ispra.

Regression analysis showed that the NPL standard agreed to within one percent of the JRC standard over five concentrations (in the range 0 to 200 ppb), with a zero offset of 1 ppb. Similar agreements were found with most other national standards.

In June 1996, the NPL ozone standard was intercompared with that of RIVM in the Netherlands. Over the range 0 to 250 ppb, the two standards showed agreement to well within one percent, with a zero offset difference of less than 1 ppb.

UK ozone measurements should therefore be compatible to within a few percent of other, similarly operated European ozone networks.

3.2.5 Rescaling of PORG Network Data, 1992 to 1994

Ozone data are scaled, (i.e. multiplied by a factor which best represents the sensitivity of the particular analyser) by the QA/QC Unit as part of the data ratification process. Scaling factors are derived primarily from the photometric calibrations carried out before and after the twice yearly analyser service at each monitoring site. These data, and data from the other sources such as daily autocalibrations, maintenance engineer reports and routine local site operator calibrations, are reviewed and discussed by a team of QA/QC unit scientists. The purpose of this review is to define the optimum scaling factors, zero offsets etc., to be used and to evaluate whether or not the data meet stringent data quality criteria or, if they do not, the extent of poor quality data which has to be deleted from the database.

Careful use of the calibration data by the QA/QC unit during data ratification generally ensures that, once the data have been ratified, they are not subsequently altered or withdrawn. During the period 1992 to 1994, however, data had to be rescaled after ratification, following additional calibration information not available at the time of their initial ratification.

Successive calibrations, relating the accuracy of the "travelling" ozone photometer used in network intercalibrations to that of other calibration standards, showed that the travelling photometer used during

the period 1992-1994 consistently under-read by *ca* 5%. As this represented a significant bias in the ratified results compared with the quoted uncertainty of ± 5%, PORG decided that all data collected during the period from April 1992 to October 1994, when the particular reference photometer had been used, were to be rescaled by + 5% (i.e. all data should be multiplied by 1.05) to account for the error.

The transition period after 1/10/94 was adjusted in the following way: For the period 1/10/94 to the date of the Autumn 1994 intercalibration exercise at each individual site the data were rescaled by a factor of 1.05, as for the main rescaling period.

For the period from this intercalibration of 31/12/94 any scaling ramp used the adjusted Autumn 1994 calibration as the starting point, and the unaltered Spring 1995 calibration, carried out with the NPL photometer, as the end point. This methodology was extended into the period from 1/1/95 to the Spring 1995 intercalibration exercise.

From the Spring 1995 intercalibration exercise to date, data have been scaled using the relevant post and pre-service intercalibration data, derived from the use of the NPL photometric standard.

3.3 Ozone Concentrations

The hourly mean ground level concentrations of ozone in the UK vary between 0 and 150 ppb, but generally lie in the range 10 to 30 ppb. To illustrate the variability in time and between contrasting sites, data for 3 monitoring stations are presented in Figure 3.2. These data provide the maximum and minimum hourly concentration for each day of the year.

Days with a concentration maxima in excess of 50 ppb can be taken to imply photochemical episodes, when the ozone concentration is raised above the background level by a combination of anthropogenic precursor emissions and weather conditions. The number of these days at the three sites, ranges from 30 days at Dunslair Heights in Central Scotland to 50 days at Yarner Wood in Southern England. The peak concentrations during these days also differ, with a maximum at Yarner Wood of 108 ppb while the equivalent value at Dunslair Heights was 78 ppb.

The episode days occur almost exclusively during the summer months (April-September) and individual episodes are often a sequence of 2 to 7 days, as can be seen at Yarner Wood on the 28th June to the 3rd July (Figure 3.2).

These high ozone days are generally sunny, warm summer days with wind advecting ozone precursors from source regions in central or northern Europe (PORG, 1987). The production rate of ozone in 'typical' conditions is often in the range 2-5 ppb per hour in the central 6-8 hours of the day so that with typical windspeeds of 2 ms^{-1} the episodes observed are the result of chemical processes at considerable (100-500 km) distances upwind. There is also an annual cycle with a spring/summer maximum which is considered in more detail later in the chapter.

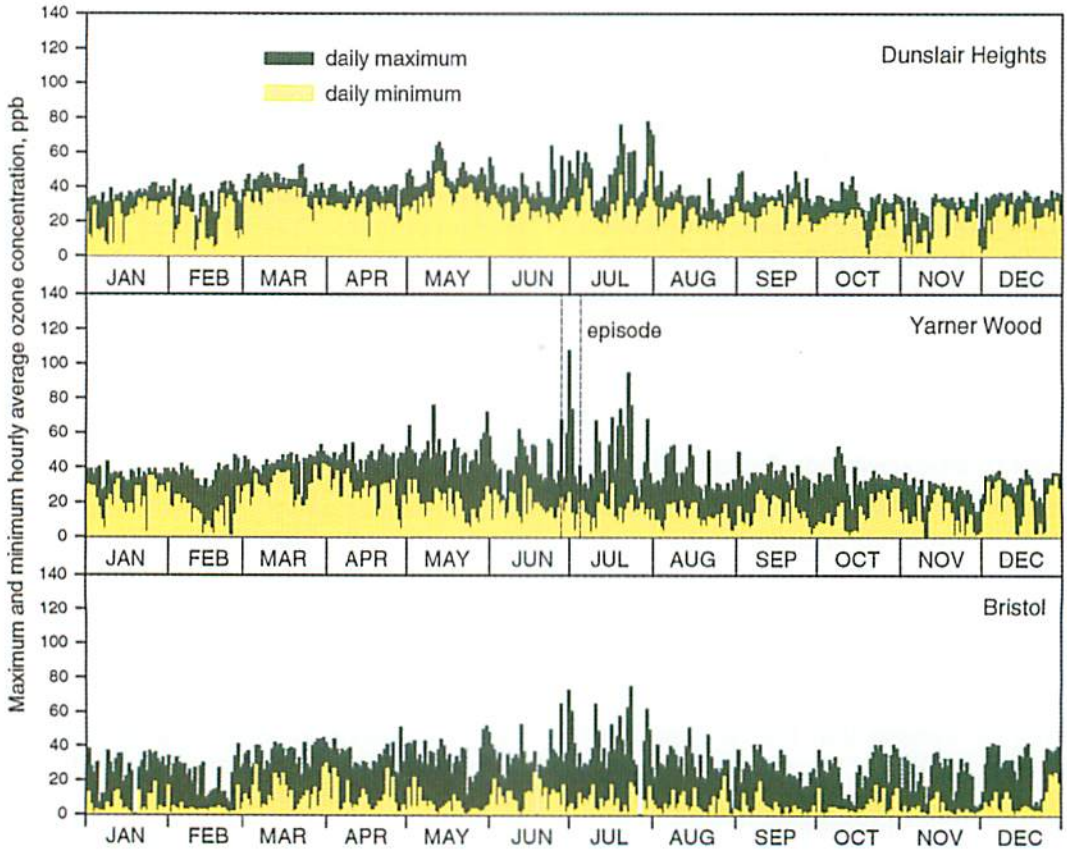


Figure 3.2 Hourly averaged maximum and minimum ozone concentrations for each day of 1994 at three monitoring sites: Dunslair Heights in central Scotland, Yarner Wood in Devon and an urban site, Bristol.

Also evident in these data are days during which ozone concentrations do not exceed 10 ppb. For Dunslair Heights and Yarner Wood the daily maximum is never smaller than 10 ppb. The data for Bristol, an urban monitoring station in the city centre, has many more (19 days) for which the maximum ozone concentration failed to reach 10 ppb as a consequence of local depletion of ozone by nitric oxide. Also plotted in these figures is the minimum hourly mean concentration for each day of the year, and it is clear that for the remote and windy northerly site at Dunslair Heights, the minima are typically 10 ppb smaller than the maxima, while for the south coast site at Yarner Wood, the minimum values are generally 20 ppb smaller than the maxima and are much smaller than those at Dunslair Heights. The larger daily range in concentration at Yarner Wood results from the lower windspeeds and greater nocturnal depletion of ozone by dry deposition and would be typical of much of central and southern England.

The data for Bristol show that at this site, ozone concentrations are reduced almost to zero for at least an hour on most days of the year. Such effects are a feature of ozone concentrations at urban sites and those close to major roads. However, even at an urban site, where local sources of nitric oxide lead to local ozone depletion, the daily maxima still achieve large concentrations during episode conditions, with values as large as 93 ppb being recorded in Bristol during 1995.

3.3.1 Effects of Windspeed

The relationship between ozone concentration at the surface and windspeed is not straightforward. However, at low windspeeds the depletion of ozone by dry deposition to the ground may exceed the downward diffusion of ozone and in these circumstances surface ozone concentration declines. This is the cause of the nocturnal depletion of ozone at unpolluted rural locations (Garland & Derwent, 1979). The effect is illustrated by examining the variation in ozone concentration with windspeed at a rural site (Figure 3.3). From the data in Figure 3.3, it is clear that when windspeeds are below 4 ms^{-1} local depletion significantly influences the concentration at the monitoring height (in this case 8.4 m). Provided windspeed exceeds 4 ms^{-1}, the effects of dry deposition on surface concentrations are small.

3.3.2 Effects of Altitude on Ozone Concentration

The effects of wind on ozone concentration illustrated above, are to reduce the effects of depletion at the ground on surface concentrations. As windspeeds and turbulent mixing processes are enhanced on hills, it follows that surface depletion effects are smaller on hills than at sheltered lowland sites. The effect is illustrated by neighbouring monitoring stations which differ substantially in altitude, as an example Dunslair Heights and Bush Estate differ by *ca* 420 m in the vertical yet are within 20 km horizontally. These show almost identical concentrations during the period 1200-1800 in summer (Figure 3.4a) while the night time concentrations differ by 25% or more. The same effect

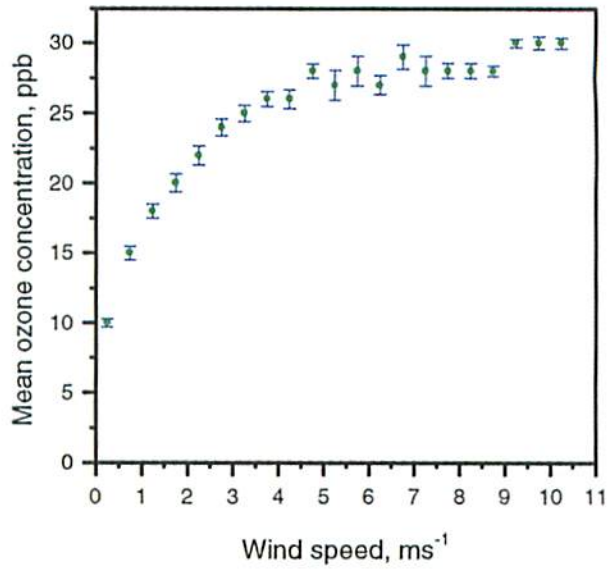


Figure 3.3 Average ozone concentration versus windspeed at Bush during November 1991 to January 1992, standard error bars shown.

may be observed in data from Wharley Croft and Great Dun Fell in Cumbria, sites separated by 10 km in the horizontal and about 600 m in the vertical, (Figure 3.4b).

These effects may be seen in the whole network when the ratio of the amplitude in the diurnal cycle is divided by the daily mean, as described in PORG 3 (PORG, 1993). The diurnal index ranges from values of 0.4 to 0.5 for remote locations at which the diurnal cycle

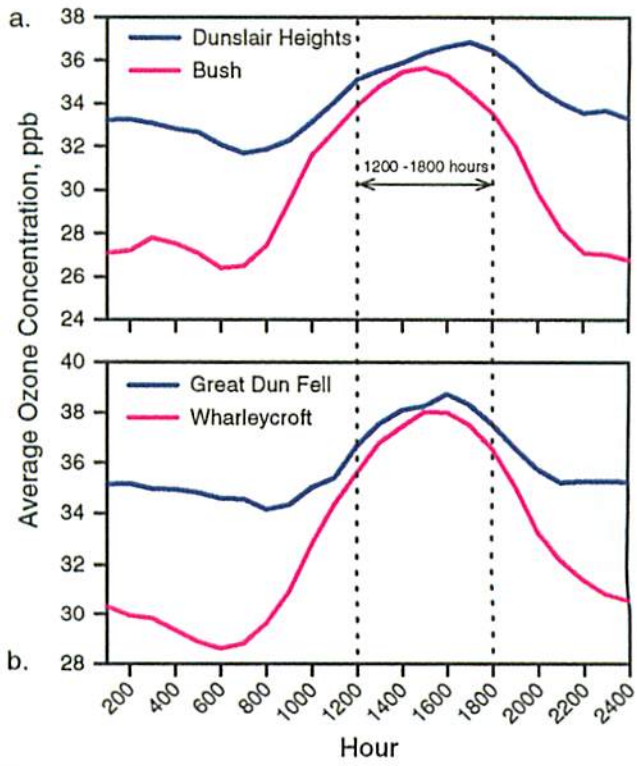


Figure 3.4 The effects of altitude on ozone concentration at, a. Dunslair Heights and Bush, and b. Great Dun Fell and Wharleycroft, during April to September 1994.

is small, and these are windy, often upland locations (Table 3.3). As the processes which regulate the surface concentrations at rural sites include both the turbulent supply of ozone from above (and hence windspeed) and deposition at the surface, surfaces with greatly reduced uptake (e.g. open water) also show small diurnal cycles, especially if they are also relatively windy exposed sites such as the coast. The diurnal index at rural sites (Table 3.3) therefore incorporates both of these effects.

The very similar concentrations during the period of the day with the most effective vertical mixing for neighbouring monitoring stations, shows that during this period the monitoring station is providing data which are representative of a much larger geographical area than during the night when local effects of shelter etc. generate great horizontal variability.

3.3.3 Effects of Proximity to the Coast on Ozone Concentration

The deposition velocity of ozone to water surfaces is only about 1 mm s^{-1}, so that vertical gradients of ozone concentration in the maritime boundary layer are small. As this air crosses a coast and moves inland, the much larger deposition rates to the land surface lead to larger vertical gradients and a drop in ozone concentration near the surface. During daytime, in the summer half of the year, a relatively deep boundary layer with efficient vertical mixing is present over land, whereas at night a shallow stable internal boundary layer (Garratt, 1992) develops, which grows only slowly with distance travelled inland. This nocturnal boundary layer may have a depth of only a few tens of metres after travel inland of tens of kilometres. The daytime mixing ensures relatively small vertical gradients of concentration, but at night the small depth and reduced vertical mixing leads to large vertical gradients and considerably reduced surface concentrations. Thus we expect a difference in the exposure to ozone between the coast and inland during on-shore flow, with essentially a constant value of concentration at the coast throughout the 24-hour period, but a pronounced diurnal variation inland, with an amplitude which increases with distance from the coast. Observations of ozone concentration from suitable coastal sites can be used to quantify this coastal effect.

An investigation ideally requires data from several sites at different distances inland along a flow trajectory from sea to land. Very few ozone monitoring sites are situated close to the coast, but four sites suitable for investigation are shown in Figure 3.5.

The site at Mace Head in the Irish Republic is on the coast and receives on-shore winds from all directions between about 230° and 270°, while the site at Lough Navar in Northern Ireland is well inland for these same flow directions. Thus these two sites form a suitable pairing for determining the average diurnal cycles of ozone concentration at the surface for flow from these directions. Similarly the sites at Weybourne and Sibton in Norfolk form a suitable pairing for all flow direction between 340° and 070°. No truly coastal data exists

Table 3.3 Listing of sites average diurnal index (index = daily range/daily mean of hourly averages), average of all sites and years on the PORG database. RR ≡ remote rural, R ≡ rural and U ≡ urban.

Site name	Type	Altitude, m	Index
Mace Head	RR	15	0.39
Strath Vaich	RR	270	0.43
Dunslair Heights	R	600	0.47
Great Dun Fell	RR	847	0.60
Clatteringshaws	R	180	0.70
Aston Hill	R	370	0.71
East Kilbride	U	50	0.82
Yarner Wood	R	119	0.84
Wray	R	100	0.84
Wharleycroft	R	206	0.86
Eskdalemuir	R	269	0.87
Bush, Penicuik	R	180	0.89
High Muffles	R	267	1.01
Ladybower	R	420	1.03
Lullington Heath	R	120	1.06
Devilla	R	80	1.08
Lough Navar	R	130	1.08
North Norfolk	R	98	1.11
Chilworth	R	80	1.14
Harwell	R	137	1.18
Sibton	R	46	1.20
East Mailing	R	32	1.30
Dursley	R	160	1.38
Syda House	R	308	1.40
Stodday	R	10	1.43
St. Osyth	R	5	1.49
Hazelrigg	R	91	1.59
West Burton	R	4	1.59
Yorkminster	U	50	1.61
Ascot	R	65	1.64
Jenny Hurn	R	4	1.66
Thorney	R	8	1.73
Lincoln	U	54	1.77
Bottesford	R	32	1.78
Glazebury	R	21	1.78
Brampton	R	6	1.79
Chigwell	U	52	1.79
County Hall	U	27	1.80
St. Bartholomew's	U	15	1.80
Nat West Tower	U	204	1.81
Canvey Island	R	3	1.85
Harrow	U	60	1.93
Hainault	U	44	1.94
Fawley	U	30	1.95
Kew	U	10	1.95
Teddington	U	20	1.96
Stevenage	U	90	1.99
Bridge Place	U	20	2.00
Glasgow	U	40	2.01
Central London	U	20	2.71
Cardiff	U	10	2.78
Cromwell Rd	U	20	2.92
Islington	U	20	4.05

Figure 3.5 The sites used for the analysis of the coastal effect on ozone concentrations, MH - Mace Head, LR - Lough Navar, WY - Weybourne, SB - Sibton.

for investigation of flow from the south-east or south.

For each of these two pairs, for the period of coincident data, days with flow from the appropriate sectors were identified from synoptic charts by assuming geostrophic flow. Only days were selected which had flow lying within these directional sectors for some distance upwind. This therefore excludes occasions of northerly flow at Weybourne which involve air which has earlier passed over the northern part of the UK. The average diurnal cycles of concentration during the summer (April-September) for on-shore flow for these two pairs of observing sites are shown in Figure 3.6.

The average cycles for Mace Head and Lough Navar for 57 days of flow from the south-western sector (230°-270°) are shown in Figure 3.6a. There is almost no diurnal variation in concentration at Mace Head, but by the time the airflow reaches Lough Navar, deposition to the land surface leads to a marked reduction in concentration at night, but a much smaller reduction in the afternoon, consistent with a deeper, well-mixed, daytime boundary layer. The average difference in concentration between the two sites is 6.9 ppb.

The average cycles observed at Weybourne and Sibton for 20 days of flow from the north and north-east (340° - 070°) are shown in Figure 3.6b. There is a diurnal cycle with an amplitude of 4 ppb at Weybourne, but an amplitude of 12 ppb at Sibton. During the afternoon the concentration difference between the two sites is only 1 ppb, but averaged over 24-hours the difference is 4.8 ppb.

Thus for the two sectors studied, observations indicate that the coastal-inland difference in mean concentration during on-shore flow is about 5-7 ppb for flow from the Atlantic and from north and north-east. Data are not available to quantify the magnitude of the coastal-inland difference in concentration for flow from the south or south-east, but it is likely to be at least as large as that found for other directions. It is with flow from the south-east that the largest ozone concentrations are observed, and weather conditions are more likely to have clearer skies and lighter winds than westerly flow. For all of these reasons it is likely that the reduction in near-surface concentrations inland, compared to the coast, will be large for south-easterly flow.

These estimates of coastal-inland differences for on-shore flow (about 6 ppb for all on-shore flows) can be combined with statistics on flow directions to give estimates of the coastal-inland difference in summertime (Apr - Sept) mean ozone concentration. A geostrophic wind rose for the UK (Jones, 1981) was used here. Clearly, sites in river estuaries are exposed to on-shore flow from only a small range of directions, whilst headlands are much more exposed to maritime air. Thus along any particular stretch of coastline the enhancement of mean ozone concentration above the inland value is spatially variable. The results found in this study

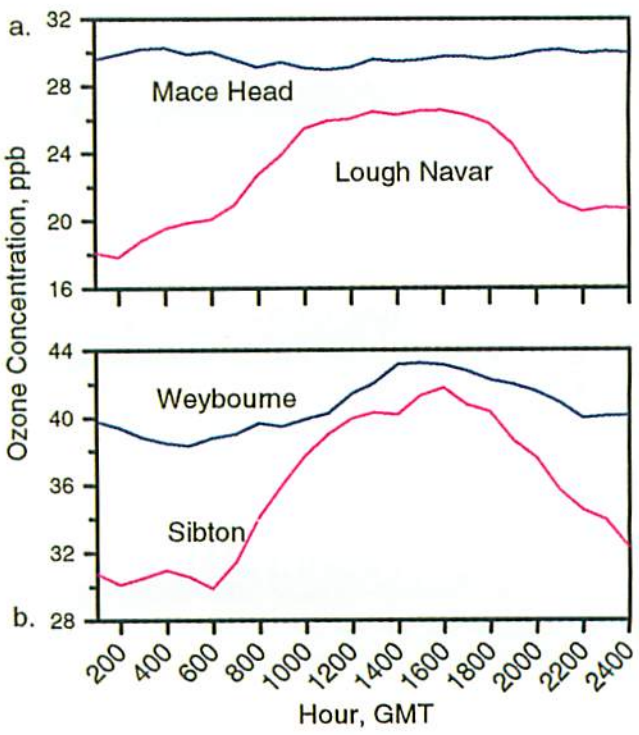


Figure 3.6 Average diurnal cycles of ozone concentration for the two pairs of stations shown in Figure 3.5. Figure 3.6a is for 57 days of coincident data from Mace Head and Lough Navar; Figure 3.6b is for 20 days at Weybourne and Sibton. All data are for the April to September period.

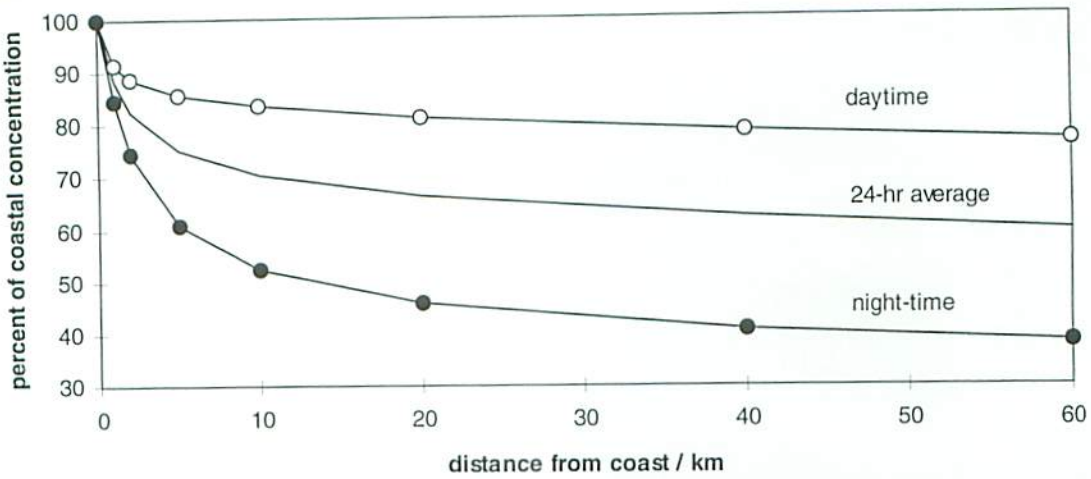


Figure 3.7 Typical variations with distance from the coast of daily-mean, daytime (12-18 hrs) and night-time (22-04 hrs) concentrations, expressed as a percentage of the coastal concentration, given by the TERN model. This model run was for a cloud cover of 4 octas, a geostrophic wind speed of 8 ms^{-1} and a deposition velocity of 5 mms^{-1}.

indicate a general enhancement of the daily-mean concentration of 2-3 ppb. The enhancement on headlands can be as much as 5 ppb, while in river estuaries it can be less than 1 ppb.

The spatial extent of enhanced concentration at the coast

Although observations have led to estimates of the magnitude of the coastal effect, they are inadequate to give any estimate of its spatial extent. However, a numerical model of the deposition process which can simulate the transitional boundary layer characteristics as air moves inland can be used to indicate the fall-off of mean concentration as the air travels inland.

The model used is a simplified version of the TERN model, described by ApSimon *et al,* 1994. Air columns, representing the mixed layer, are initialised at the coast with a vertically uniform value of ozone concentration and advected inland with the geostrophic

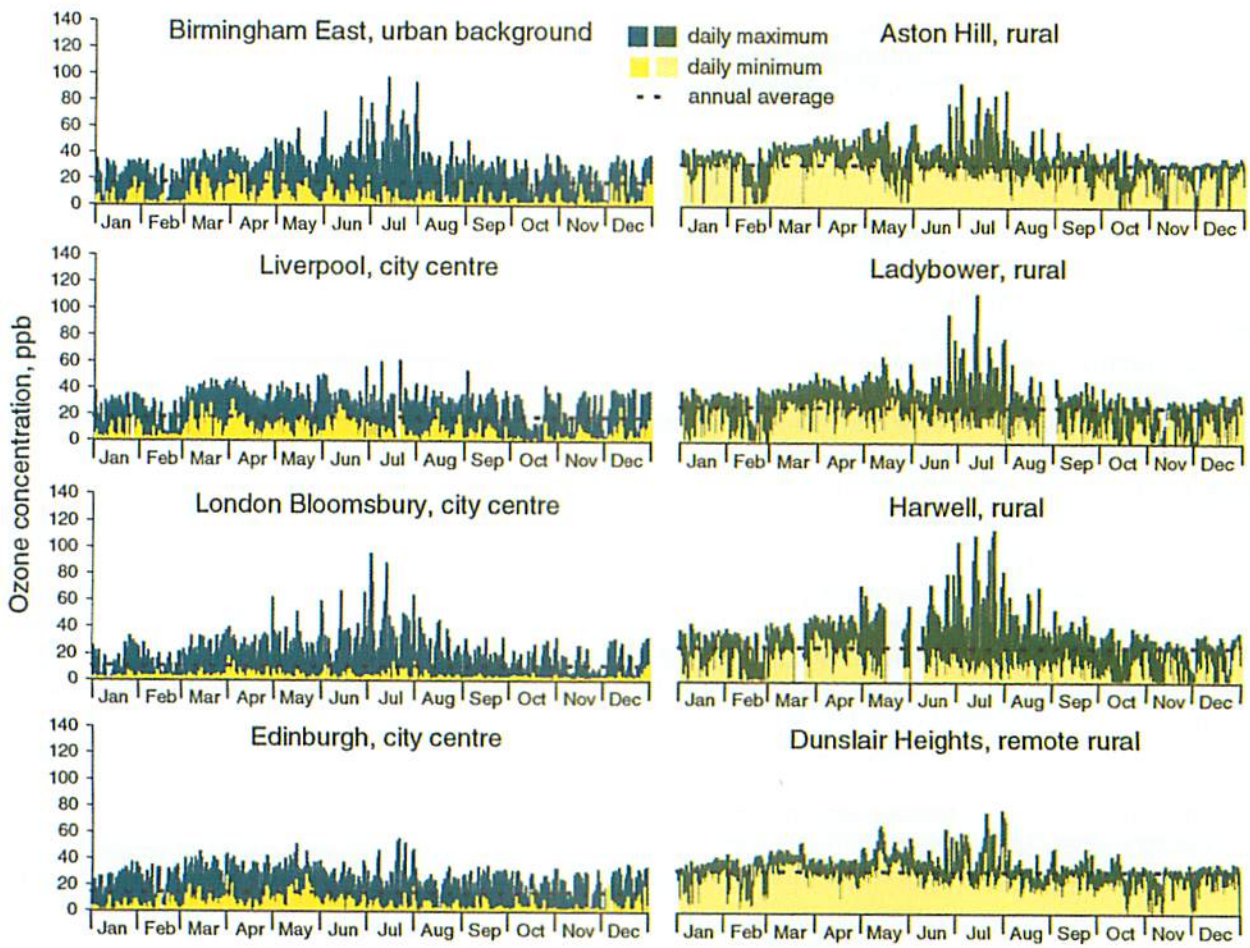


Figure 3.8 Daily maximum and minimum hourly average ozone concentrations at eight sites, contrasting urban and rural levels.

speed. Ozone chemistry is neglected. This is justified on the small time-scale of flow within a few kilometres of the coast. Deposition over land is modelled with a deposition velocity which is assumed to be spatially uniform and constant in time with a value of 5 mm s^{-1}. The air columns are divided into 33 layers and vertical mixing is described using K-theory eddy diffusivity. The percentage decrease of concentration at a height of 3 m as a function of distance from the coast for a geostrophic speed of 8 m s^{-1} and half cover of cloud is shown in Figure 3.7.

Shown separately are the concentration profiles for the well-mixed period (12-18 hrs) for night-time (22-04 hrs) and for the entire 24-hour period. As expected, there is a greater decrease over land at night than during the daytime, due to considerably reduced vertical mixing. All three profiles show the coastal-inland difference in concentration to be concentrated in the first few kilometres, with half of the change between the coast and 60 km inland occurring in the first two kilometres. Sensitivity studies show that this result is rather insensitive to changes in cloud cover, flow speed, mixing depth and deposition velocity.

3.3.4 Ozone in Urban Areas

Ozone concentrations in urban areas are generally much lower than in the surrounding countryside due to the reaction of ozone with nitric oxide [i], which generates NO_2, see Chapter 2 for details. The main source of NO in populated areas is from vehicle exhaust emissions, although other sources add to ambient levels, see Chapter 6.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad [i]$$

The effect of this reaction can be seen in Figure 3.8 which shows the daily maximum and minimum hourly ozone concentrations and annual mean hourly concentration for 4 UK city centre locations, with estimates of the rural concentrations nearby. These show broadly similar general features of low ozone concentration in urban areas with the annual mean ozone concentrations much smaller than those in the surrounding countryside, being often only 30% to 50% of the rural values. However, during some photochemical episodes the hourly average ozone concentration in a city may reach high levels similar to those in the surrounding countryside, see Figure 3.9.

Figure 3.10 also illustrates the effect of NO emissions by contrasting data from three monitoring stations along a 30 km transect from city centre to a remote upland site: Edinburgh City Centre, Bush Estate 10 km south of Central Edinburgh, a rural site but close to the town of Penicuik; the summit of Dunslair Heights at an elevation of 600 m, 30 km south of Edinburgh City Centre.

The data for 1994 in Figure 3.10 show the annual average diurnal cycle in ozone concentration at these three stations. The hill summit shows only a small amplitude of 2 ppb in the diurnal cycle in concentration with a mid afternoon maximum at the time of the maximum in turbulent mixing. At Bush Estate the diurnal amplitude is larger at about 6 ppb, with essentially the same maximum as Dunslair Heights during the afternoon. By contrast, the Central Edinburgh site shows the smallest concentration of the 3 stations with the maximum during the hours of the morning 0100 to 0500 when traffic density and the nitric oxide emissions from vehicles are at a minimum.

The minimum concentration is at the morning 'rush-hour' 0800-0900 with concentrations of about 10 ppb ozone while those in the countryside at the same time are 15 to 20 ppb larger. Because ozone depletion in the city is largely a consequence of the reaction with nitric oxide to produce NO_2 and is the major source of NO_2, the NO_2 concentrations are often of a similar magnitude in cities to the difference in ozone concentration between the countryside and the town centre.

Wind speed also has an effect on urban ozone concentrations, as shown at the Edinburgh city centre site in Figure 3.11. At high wind speeds ozone is advected into the city from the surrounding rural areas as the atmosphere becomes more mixed, increasing the ozone concentration. At the same time NO emitted by

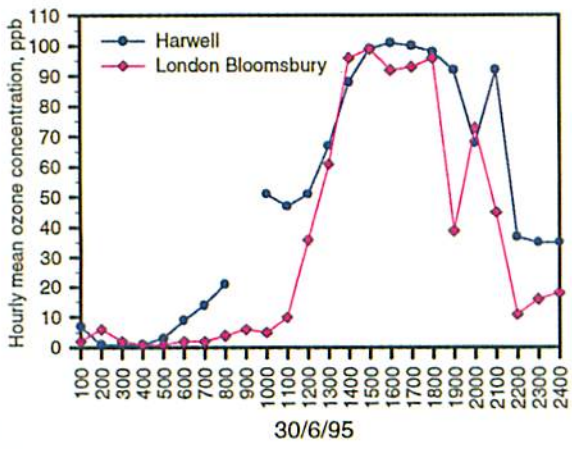


Figure 3.9 Hourly average ozone concentrations at Harwell and London Bloomsbury on the 30th June 1995.

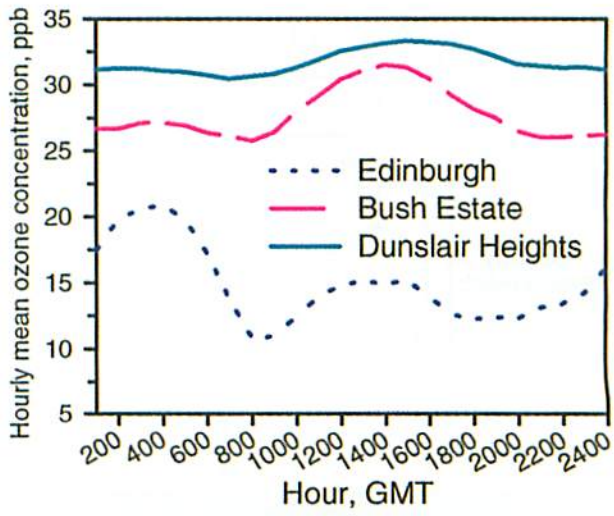


Figure 3.10 Average diurnal cycles for 1994 at three sites, Dunslair Heights at 600 m and 30 km south of Edinburgh, Bush Estate at 180 m elevation and 10 km south of Edinburgh and an urban site Edinburgh.

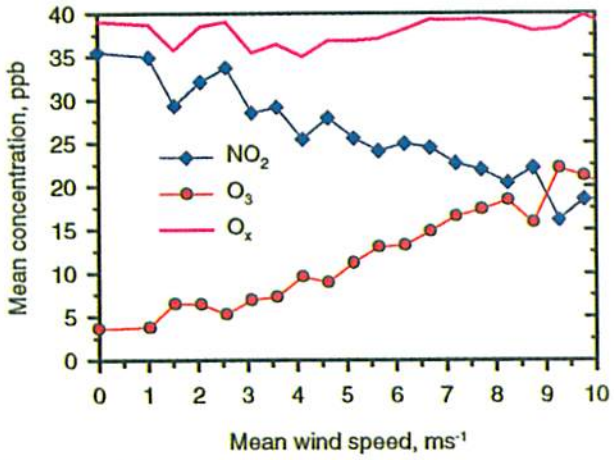


Figure 3.11 The mean concentrations of ozone, NO_2, and O_x (= O_3 + NO_2) with wind speed in Edinburgh, Nov. - Dec. 1994.

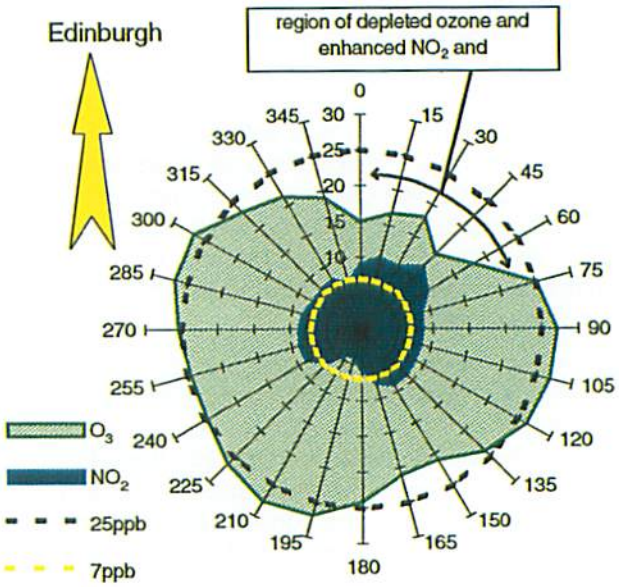


Figure 3.12 Average ozone and NO_2 concentrations versus wind direction at Bush during 1992.

vehicles is diluted in the well mixed air and so less of the ozone is destroyed by the reaction with NO, reducing the NO_2 concentration. The fairly constant value of O_x, the sum of O_3 and NO_2, shows that most of the NO_2 in urban air is a consequence of O_3 depletion.

The emissions of NO from urban areas can also have an effect on the ozone concentration at rural sites close by, when polluted air is carried out of the city into rural areas. This can be seen in the measurements of NO_2 and O_3 at Bush when they are plotted against wind direction, Figure 3.12. When the wind is coming from Edinburgh and surrounding industrial areas, the ozone concentration at Bush is slightly reduced and the NO_2 enhanced. However, as the prevailing wind direction is from the south-west this does not happen very often and for most of the time Bush measures rural ozone concentrations. Major roads or power stations in the proximity of a rural ozone monitoring site may also affect the measured ozone concentrations in a similar manner.

3.3.5 Ozone Dry Deposition

The pronounced diurnal cycle in ozone concentration at sites unaffected by local sources of nitric oxide reveal the effects of dry deposition of ozone to the underlying surfaces (vegetation and soil). These processes are well known and have been described by Garland and Derwent (1979). The variation in dry deposition of ozone onto vegetation has been shown to be largely regulated

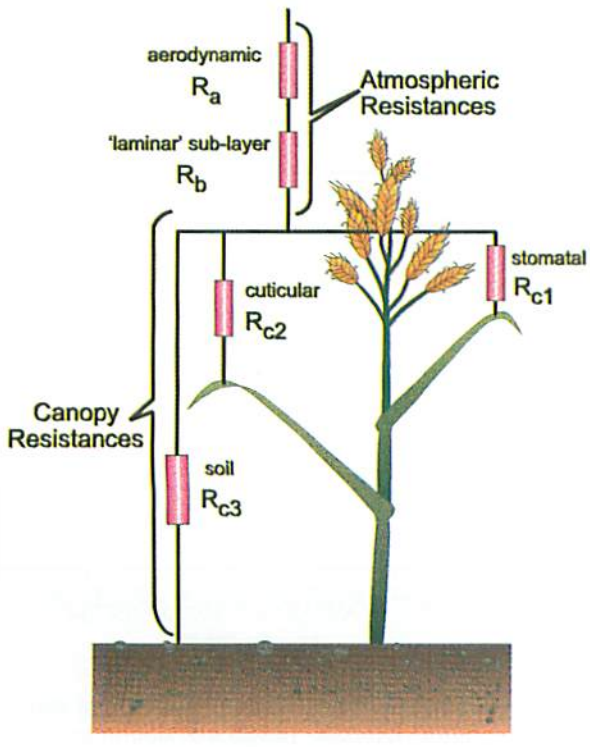


Figure 3.13 A deposition resistance analogy.

Total resistance between z and the absorbing surfaces:

$$R_t = R_a + R_b + \left(\frac{1}{R_{c1}} + \frac{1}{R_{c2}} + \frac{1}{R_{c3}} \right)^{-1}$$

Deposition velocity, v_d :

$$v_d(z) = \frac{\text{Flux}}{\text{concentration}(z)} = \frac{1}{R_t}$$

where z = reference height for the concentration, v_d and R_t

by stomatal resistance (Hargeaves *et al*, 1992) with the majority of the daytime ozone flux during the growing season being stomatal uptake. However, external surfaces of leaves also represent an important sink for ozone averaged over a year. The processes regulating deposition to the surface are generally quantified using a resistance analogy illustrated in Figure 3.13.

Using this approach, the relative importance of atmospheric transfer and surface processes are readily separated. Further separation of the different sites of uptake (sinks) for ozone at the surface are also quantified using this approach. The aerodynamic resistance R_a may be estimated directly from turbulence or wind profile measurements and is given by, (Monteith and Unsworth, 1990):

$$r_{a(z)} = \frac{U_z}{U_*^2} \quad [ii]$$

where:
U_z = windspeed at the reference height, z
U_* = friction velocity

and the quasi laminar boundary layer resistance rb is given by:

$$r_b = (BU_*)^{-1} \quad [iii]$$

where:
B (sub-layer Stanton number) = $1.45R_e^{-0.24}S_c^{0.8}$
R_e is the turbulent Reynolds number (R_e = $z_o U_*/V$) in which z_o is the lower limit of the inertial sublayer.
S_c is the Schmidt number (S_c = n/D) in which n is the kinematic viscosity of air and D is the molecular diffusion coefficient of ozone.

Over the bulk of the UK landscape, vegetation is the predominant surface at which ozone is deposited. In general the properties of all vegetation for ozone uptake are similar. The stomatal uptake may be assumed to be limited only by the diffusive resistance of the

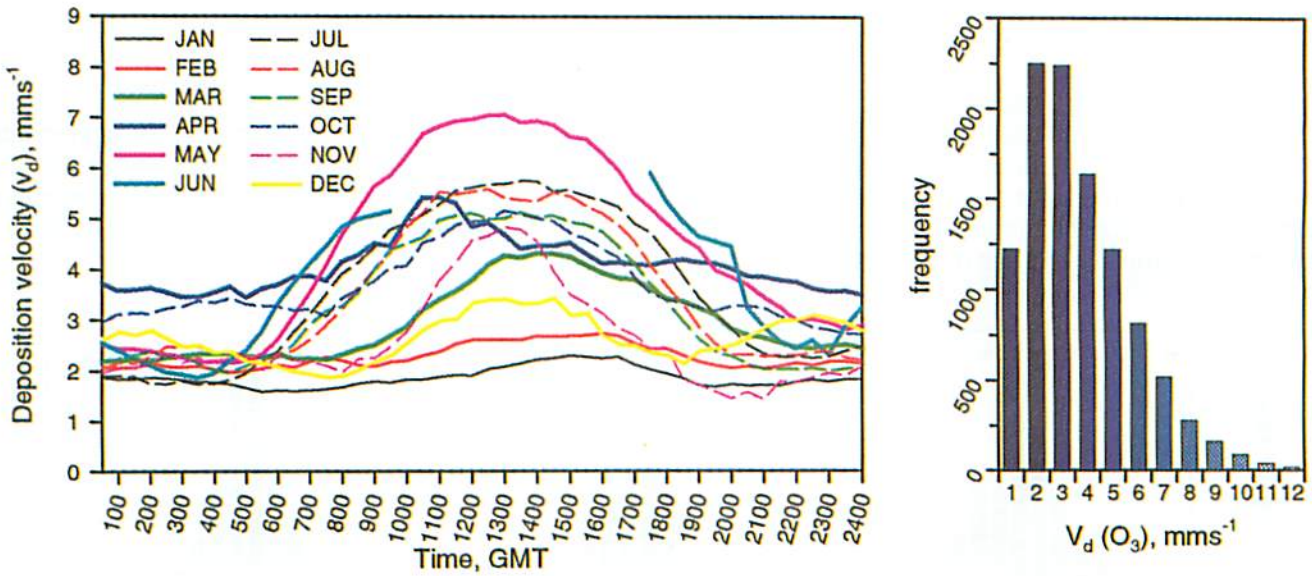


Figure 3.14 Diurnal cycles of 3 hour running geometric mean deposition velocity, v_d (mms^{-1}), at Auchencorth Moss for each month of 1994, and the frequency distribution of v_d for 1994.

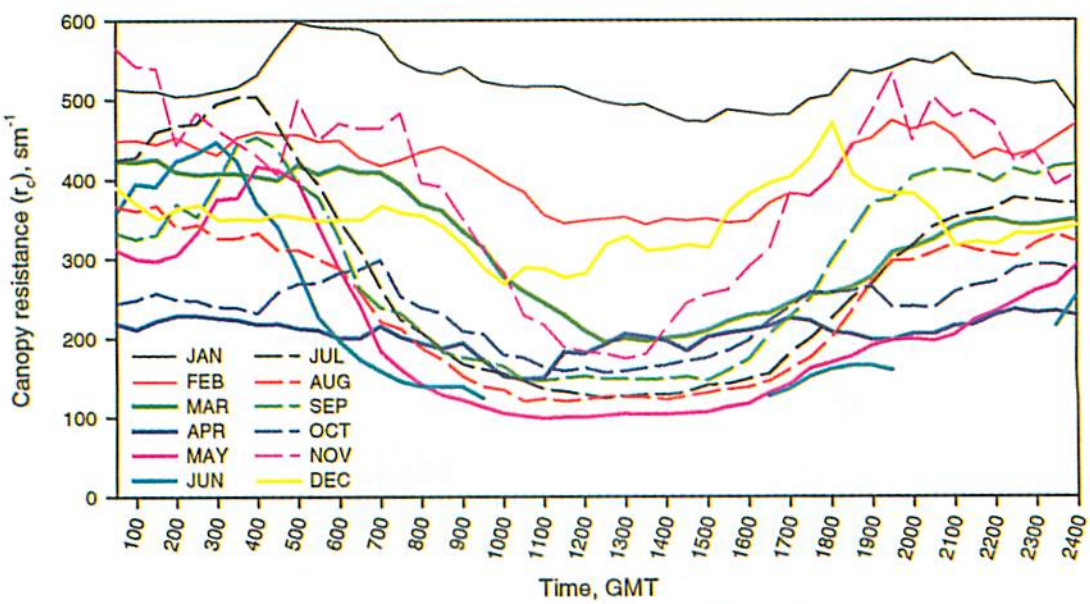


Figure 3.15 Diurnal cycles of 3 hour running geometric mean canopy resistance, R_c (sm^{-1}), at Auchencorth Moss for each month of 1994.

stomatal aperture and thus concentrations of ozone within the sub-stomatal cavity are zero (Weiser & Havranek, 1995). Vegetation does differ in the rate of ozone deposition to external surfaces. For most vegetation the external uptake leads to deposition velocities (v_d) in the range 1-3 mms^{-1} being representative of many surfaces in a wide range of conditions.

Recent continuous measurements of ozone deposition fluxes over moorland (dominated by upland grasses) show the mean characteristic of ozone dry deposition.

The data from Auchencorth Moss in the Scottish Borders show deposition velocities in the range 1.5 to 7 mms^{-1} during the 12 months of continuous measurement. The nocturnal and winter values lie in the range 1.5 to 3 mms^{-1} and over an averaged diurnal cycle the daily winter deposition velocity varies little from 2 mms^{-1} indicating an almost constant rate of deposition to the external surfaces of the mainly senescent vegetation (Figure 3.14). During the spring and early summer daytime rates of deposition are larger and values of 4 to 8 mms^{-1} are common at mid-day. When averaged for the month, a daytime maximum of 6 mms^{-1} at 1300 GMT is observed and the deposition in excess of the nocturnal values cover a time 'window' of 15 hours from 0600 until 2100 reflecting the long summer days at these latitudes (Figure 3.14). At this time of the year, approximately half of the ozone is absorbed by stomata and half by external leaf surfaces, while over the year as a whole, most of the ozone uptake occurs on the external surfaces of vegetation. These data and similar short term measurements over other surfaces (Fowler *et al* 1996, Wieser & Havranek 1995) show that the deposition process for ozone is now quite well understood and provide the necessary information to simulate ozone deposition over the countryside, generally using resistance models together with ozone concentration measurements from the monitoring networks. In assigning appropriate values for components of the resistance network, the data from Auchencorth show that the bulk canopy resistance (r_{c2}) for leaf surface ozone uptake has a value of about 320 s m^{-1} (± 30 s m^{-1}) and that the reduced total r_c values during the day are regulated by solar radiation, air temperature and saturation deficit. While a detailed treatment of the analysis lies outside the scope of this chapter, the summary data for measurements at Auchencorth Moss (Figure 3.15) show the main features of the annual and daily changes in canopy resistance for ozone over moorland.

3.3.6 Frequency Distribution of Ozone

The frequency distribution of ozone measurements at any monitoring site reflects the general ozone climate at that location and all the effects described in the previous sections can influence the shape of the distribution.

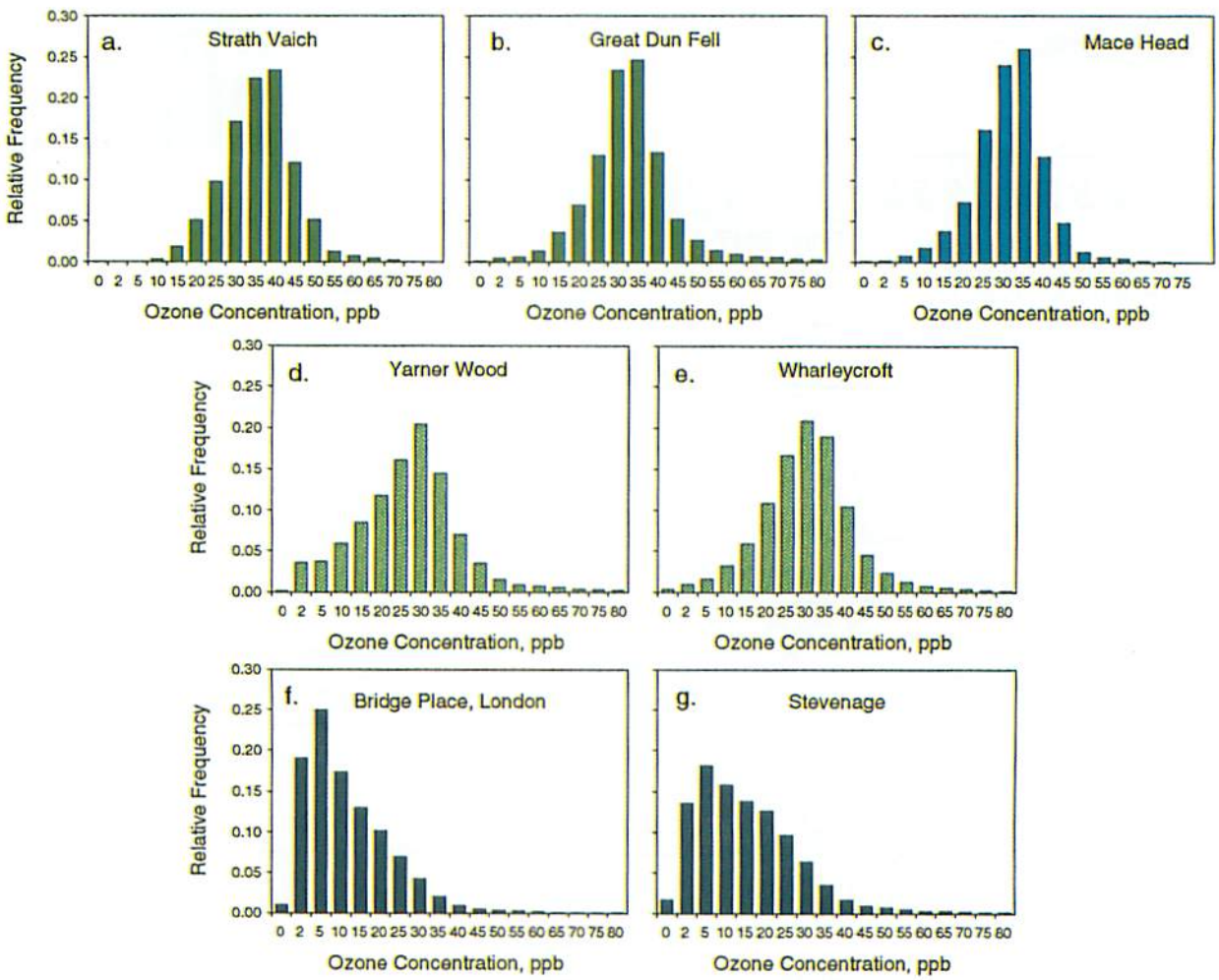


Figure 3.16 Average frequency distributions for 1988 to 1995 as available, at a selection of network sites.

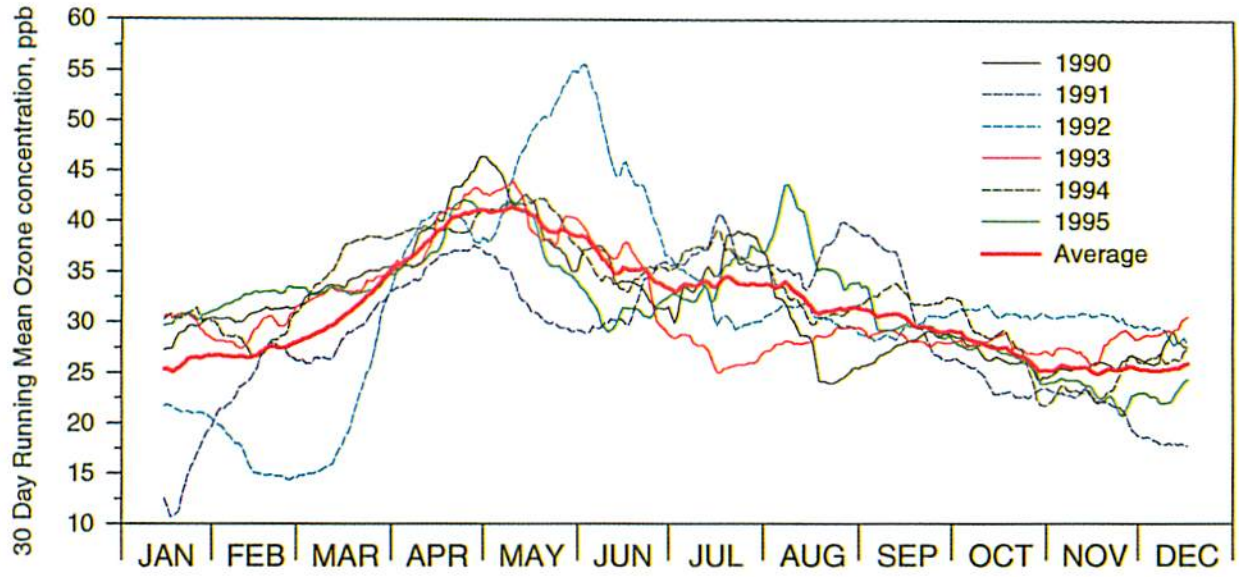


Figure 3.17 Annual and average 30 day running means of hourly average ozone concentrations at Great Dun Fell.

The ozone concentration measurements at sites such as Strath Vaich and Great Dun Fell show an approximately normal distribution with a small standard deviation, (Figure 3.16 a and b).They are remote, windy sites, with a small amplitude in their diurnal cycle, as there is little nocturnal depletion of ozone by dry deposition and very little NO pollution to reduce ozone concentrations. Mace Head also has a similar distribution (Figure 3.16 c) although this is because it is a coastal site which experiences onshore airflow for much of the time and therefore has very little nocturnal depletion. Rural sites in sheltered, lowland areas, such as Yarner Wood and Wharleycroft, also have an approximately normal distribution (Figure 3.16 d and e) but as there is more variation in the diurnal cycle the curve is flatter with a larger standard deviation.

Data for urban or sub-urban sites such as Bridge Place (London), and Stevenage show a very asymmetrical distribution with a substantial fraction of the time with small ozone concentrations. This is due to the reaction of ozone with nitric oxide, emitted by vehicle exhausts and other combustion processes, reducing the ozone concentration for much of the time, (Figure 3.16 f and g).

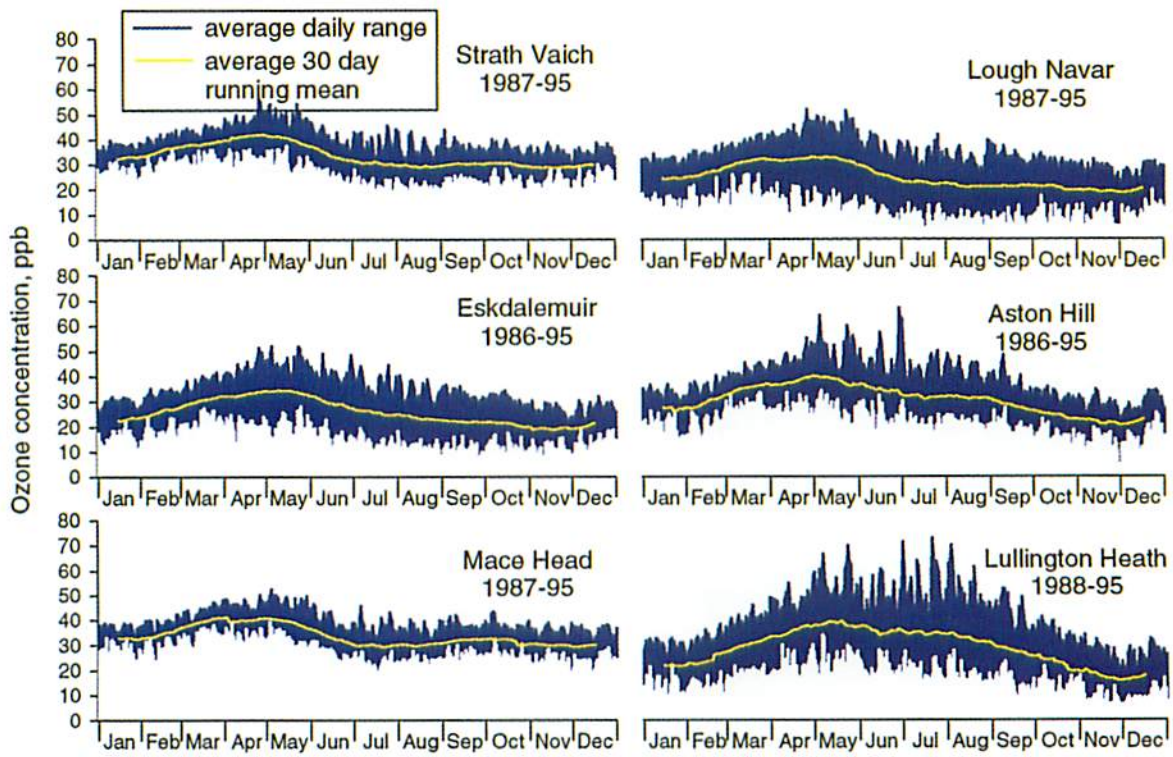


Figure 3.18 Average annual cycles as 30 day running means of the daily mean (yellow line), with the daily range plotted as the daily minimum to maximum (blue shading), at 6 rural sites.

3.3.7 Seasonal Cycles in Ozone

The annual ozone data for Dunslair Heights and Yarner Wood show a spring-summer peak in ozone concentrations which is observed widely in Europe (see Figure 3.2). These seasonal trends are more easily detected when 5 years data are smoothed, by presenting 30-day running means, as shown for Great Dun Fell (Figure 3.17). The amplitude of the annual cycle is 15 ppb from a spring maximum of 40 ppb to a mid-winter minimum of about 25 ppb. These smoothed data conceal large inter-annual differences which are shown on the same figure. Similar effects may be observed at remote rural sites and the less polluted rural sites (Figure 3.18).

3.4 Mapping Ozone Concentrations

The effects of windspeed and hence altitude on the diurnal cycle in ozone concentration and the heterogeneous nature of the landscape (Figure 3.3 and 3.4) make it difficult to interpolate between the measurements from a sparse network such as the rural ozone monitoring stations without introducing large systematic errors. In particular, a monitoring station in complex terrain only provides data for the exposure at the measurement site, so that simple interpolation between monitoring sites which fails to incorporate the effects of topography will fail to predict the actual spatial patterns in ozone exposure.

In this section the methods developed to incorporate the effects of topography into the maps of rural mean ozone concentrations and the occurrence of values which may damage vegetation and/or human health are described. The development of corrections to these maps to incorporate estimates of urban ozone exposure are also described.

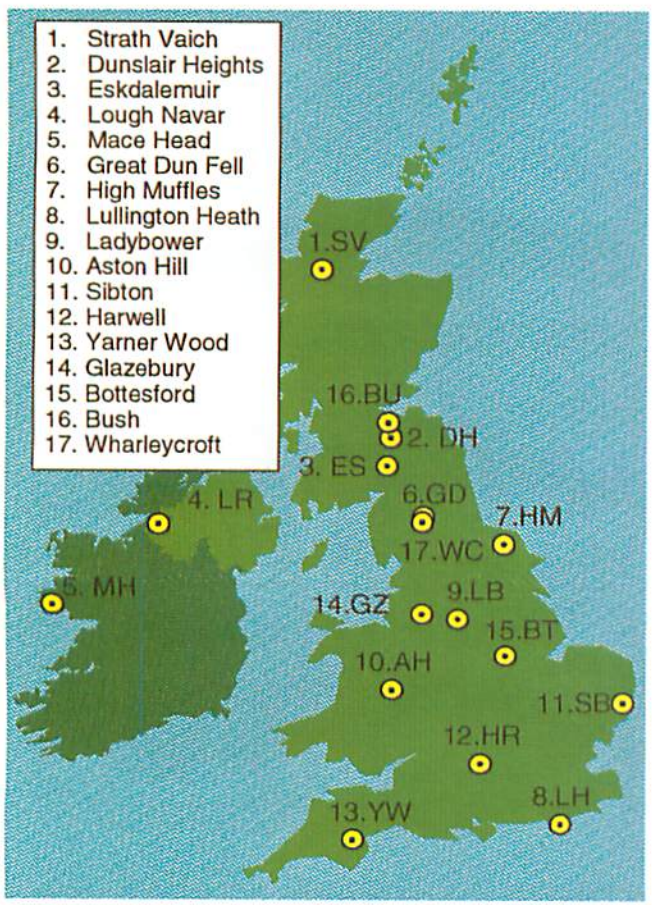


Figure 3.19 Sites used for mapping ozone values.

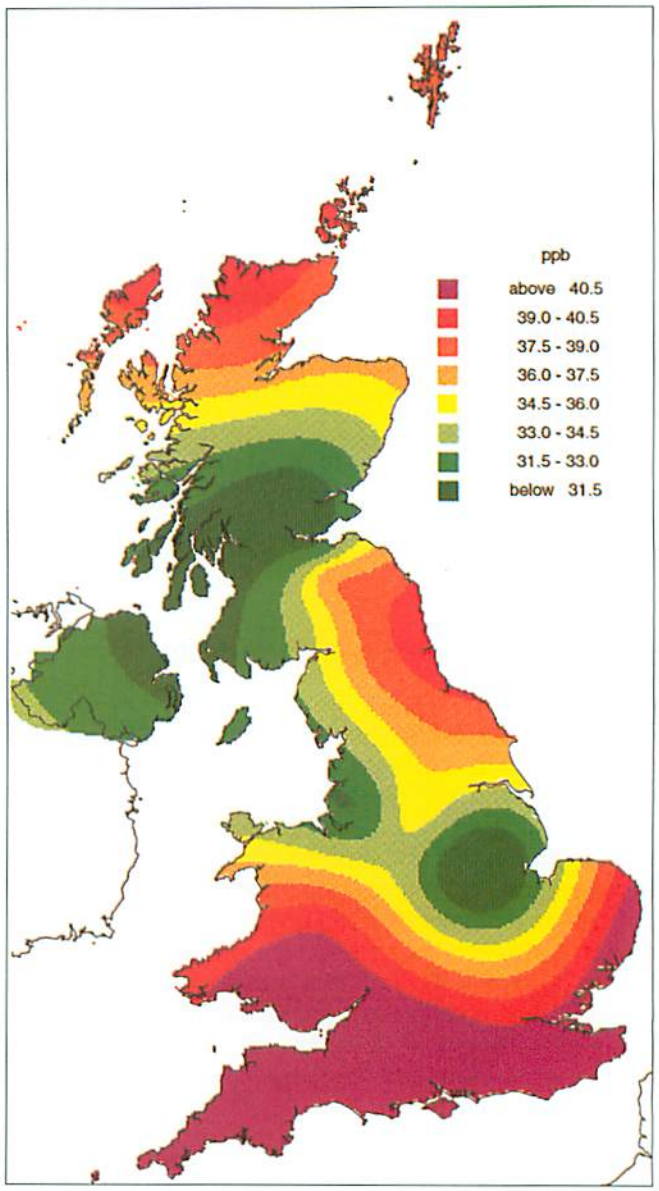


Figure 3.20 Interpolated map of 1200-1800 hour mean ozone concentration, ppb, for the summer period (Apr-Sep). Based on 1990-94 averaged data.

3.4.1 Mapping Summer Mean Ozone Concentrations

The monitoring network contains only 17 sites to define the spatial patterns and, as shown earlier, simple direct interpolation between the sites fails to predict the pronounced effect of topography on the pattern of surface ozone concentration.

However, the diurnal cycles in ozone, especially for the summer period, show that during the afternoon many of the rural monitoring stations in the same region (within 100 km of each other), show similar concentrations despite considerable altitude differences within the boundary layer. For the summer months, during which the peak concentrations are observed, the broad patterns in maximum ozone concentration may be interpolated using the 17 rural stations, (Figure 3.19). This procedure then provides a 'base' map

(Figure 3.20) on which the effect of the dry deposition at night may be superimposed. The amplitude of the diurnal cycle in ozone concentrations is related to the mean altitude of the monitoring station, with the smaller values at upland sites.

This effect is quantified in Figure 3.21a as the relationship between altitude of monitoring station and ΔO3 (the difference between the concentration during the 'well mixed' period 1200 GMT to 1800 GMT and the daily mean concentration). The data contain considerable scatter as there are many other site factors in addition to altitude which cause nocturnal depletion.

The relationship: $\Delta O3 = 3.4 + 7.7e^{-4.2 \times 10^{-3} \, altitude}$

may then be used with an altitude map of the country to obtain ΔO3 for each 1km x 1km grid square of the country.

Then by depleting an interpolated summer well mixed boundary layer mean ozone concentration map (Figure 3.20) by ΔO3 gives an April to September mean concentration map which incorporates some of the known local scale heterogeneity (Figure 3.22).

The largest concentrations are found on the uplands of southern and SW England and Wales. The clear NW-SE and altitude gradients in mean ozone concentration are evident in the map. This is, of course, a rural map and the summer mean ozone concentrations in towns and cities will generally be considerably lower than indicated by this rural map.

Interpolations over the UK from data for only 17 sites will only portray regional trends and the underlying interpolation procedure will affect the appearance of the map. For example, the relatively low concentrations mapped in West Scotland and the South West highlands reflect a lack of sites in the area. Lacking such information, the interpolation procedure extrapolates the gradients between Mace Head and Lough Navar in Ireland and between Dunslair Heights and Bush in East Scotland to give an extended area of low concentration which is probably unrealistic. Similar effects occur in many other areas. For example concentrations are probably too low in North Wales and too high in South Wales and the area of low concentration in the rural East Midlands is rather arbitrarily defined.

Effects of urban areas

Ozone concentrations in urban areas are lower than in the surrounding countryside due to the scavenging of ozone by NO emitted near to ground level by vehicular and other combustion sources, as described in Section 3.3.4. The number of ozone monitoring sites in urban areas has increased substantially since 1992, with the establishment of the Automatic Urban Network. The data from these monitoring sites enable the relationships between ozone concentrations in urban and surrounding rural areas to be investigated and maps incorporating estimates of concentrations in urban areas to be prepared for the first time. Ozone measurements are not, of course, available in all urban areas. Once the urban influence on ozone concentration has been established, the relationship between this urban influence, UI, and a surrogate statistic, such as land cover information can be used to estimate ozone concentrations in towns and cities for which measurements are not available.

An urban influence on summer mean ozone concentration can be defined as:

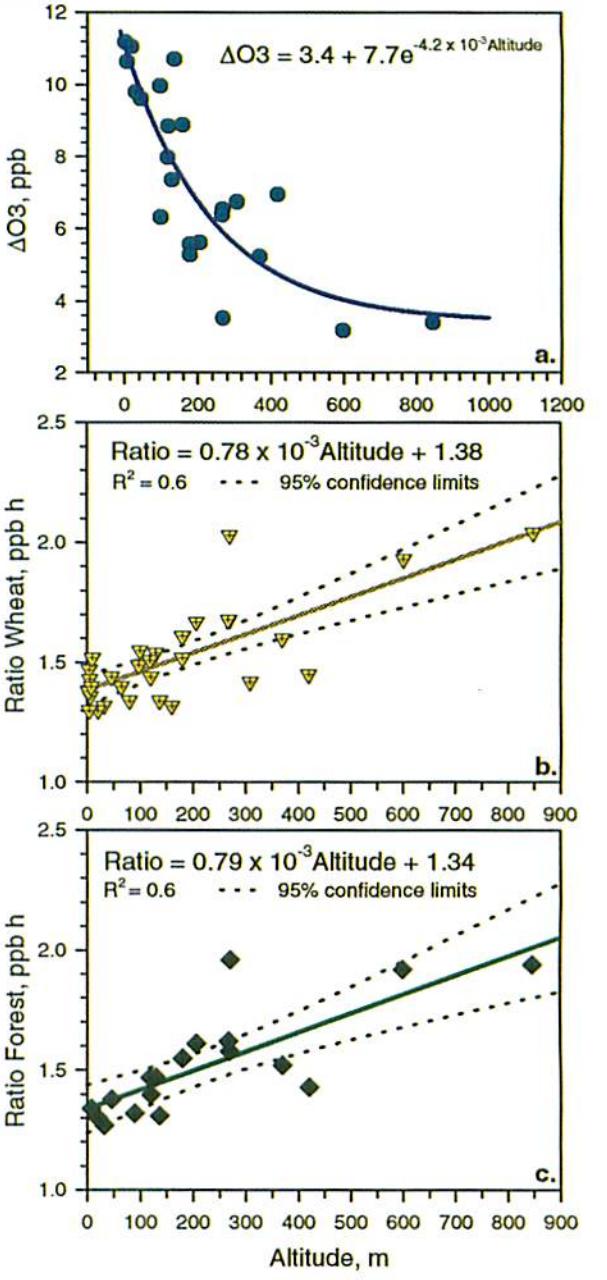


Figure 3.21 Altitude relationships used for calculating mapped ozone values:

a. ΔO3 = (mean O_3 concentration 1200-1800 hours) - (mean 24 hour O_3 concentration)

The site means of years 1975 to 1994 with data capture over 60% are plotted.

b. Ratio Wheat = $\frac{\text{AOT40 May - July daylight hours}}{\text{AOT40 May - July 1200 - 1800 hours}}$

The site means of years 1975 to 1994 with data capture over 60% are plotted.

c. Ratio Forest = $\frac{\text{AOT40 Apr - Sept daylight hours}}{\text{AOT40 Apr - Sept 1200 - 1800 hours}}$

The site means of years 1975 to 1994 with data capture over 60% are plotted.

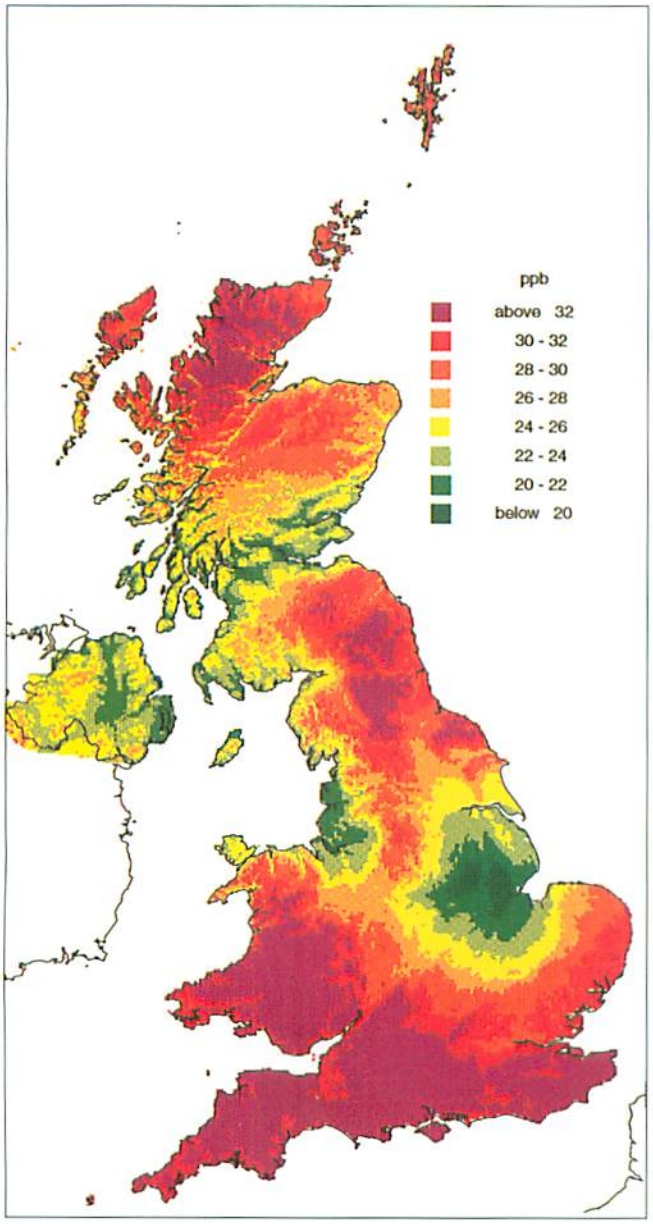


Figure 3.22 Mean ozone concentrations, ppb, during April to September, calculated from the base map shown in Figure 3.20 and is therefore based on 1990 - 94 averaged data.

$$UI = \frac{\text{((rural summer mean ozone) – (measured urban summer mean))}}{\text{(rural summer mean ozone)}}$$

where 'rural summer mean ozone' is the 5 km x 5 km grid square concentration appropriate for the urban monitoring site, interpolated (and corrected for topography) from rural measurements and 'measured urban summer mean ozone' is the concentration measured at the monitoring site. The UI for a rural monitoring site will be zero, while for an urban site, UI will have a value between 0 and 1.

The urban influence, UI for a given 5 km x 5 km urban grid square will be dependent on the magnitude of local NO emissions. A 5 km x 5 km grid square map (Fuller *et al*, 1994) of the proportion (between 0 and 1) of land cover in each square that is rural has been used in this mapping work as a surrogate for the strength of the local NO emissions. The smaller the proportion of rural land cover in each square, *rurlc*, the more urban or suburban land cover there will be and hence the more NO emissions for vehicles and other low level combustion sources there will be.

The UI for summer mean ozone concentration at each urban monitoring site is shown in Figure 3.23. Sites in central London, where the proportion of rural land cover is less than 0.2 have the highest UI, of about 0.5. Sites such as Bottesford and Glazebury, with *rurlc* greater than 0.8 but less than 1, have UI of about 0.2. The following relationship between UI and *rurlc* has a correlation coefficient, r, of 0.87:

$$UI = 0.55 - 0.55 rurlc.$$

UI therefore varies from between 0 in rural areas to a maximum value of 0.55 in a completely urban grid square. The urban corrected summer mean ozone concentration for each 5 km x 5 km grid square can then be calculated and will be given by:

summer mean ozone = (rural summer mean ozone) (1-UI)

which gives r = 0.90 for the correlation between measured summer mean ozone concentration and the 5 km x 5 km grid square estimate, where measurements are available. The resulting map is shown in Figure 3.24 and clearly shows the lower ozone concentrations in urban areas, superimposed on the rural concentration field.

3.4.2 Mapping Ozone Concentrations that are Potentially Damaging to Vegetation

The spatial pattern in mean ozone concentration is of general and academic interest but has few practical applications. However, interest in ozone as a phytotoxic agent led to the field research programmes to define the relationships between crop yield loss and ozone exposure, which are considered in detail in Chapter 7.1. In this section, the method of mapping the exposure of vegetation and forests to potentially damaging ozone exposure is developed.

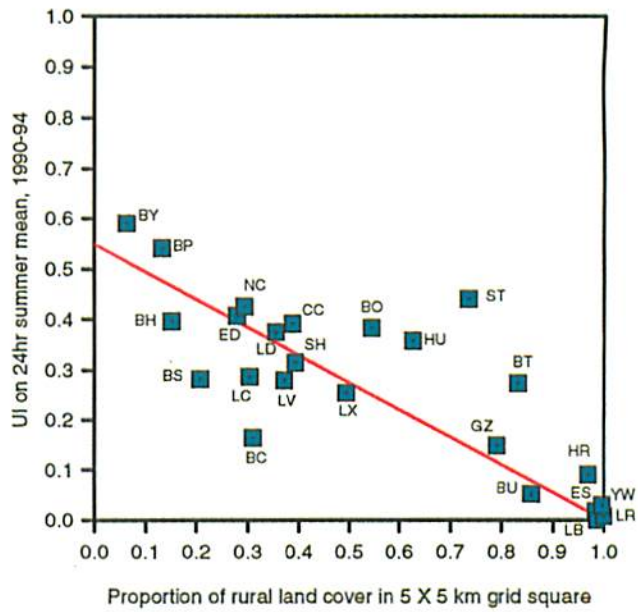


Figure 3.23 Comparison of the urban index for summer mean ozone concentrations to the proportion of rural land cover in a 5 x 5 km grid square (Fuller *et al*, 1994).

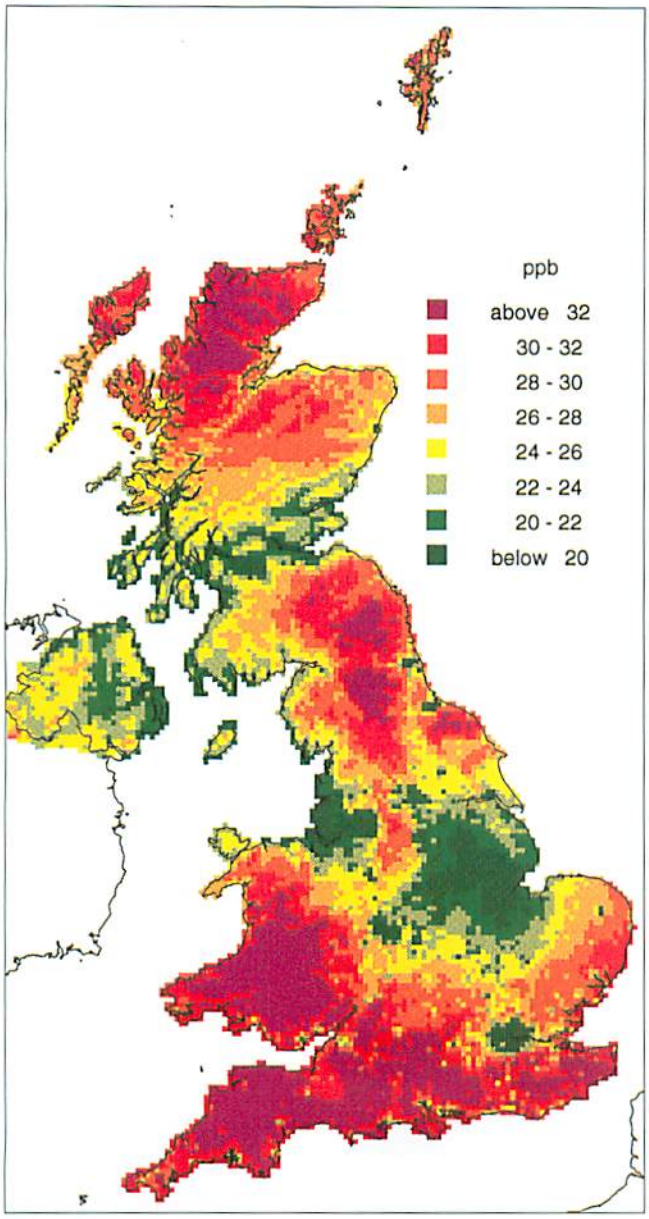


Figure 3.24 5 x 5km summer mean ozone concentrations compensated for urban influence, based on Figure 3.22. Data from J.Stedman at AEAT.

Current knowledge has led to the definition of critical levels, based on an AOT40 (Accumulated exposure Over a Threshold of 40 ppb) index, for the assessment of risk related to ozone effects on vegetation, defined in Table 3.4 and described fully in Chapter 7.1.

A similar approach for quantifying the 1 km x 1 km field in AOT40 to that developed for mean ozone concentration is adopted for wheat and for forest, although the base maps were interpolated from 16 of the rural sites, (all sites except Bush). The resulting maps are more appropriate for rural areas in Scotland, especially north of the Forth valley which is a large area without any monitoring stations. Dunslair Heights, a high elevation site only *ca* 30 km south of Bush, is less influenced by local depletion of ozone by nitric oxide and so it measures levels of ozone more representative of rural areas.

AOT40 for crops and semi-natural vegetation

The average daytime period of maximum turbulent mixing 1200-1800 is used to produce a base map of AOT40 during May - July throughout the country, as described by Fowler *et al* (1995). The map (Figure 3.25) shows a North to South gradient of increasing AOT40 from around 1500 ppb h $year^{-1}$ in Scotland to over 4000 ppb h $year^{-1}$ along the south coast of England.

To map the AOT40 value for daylight hours it is necessary to quantify the degree to which an individual grid square (mapping at 1 km x 1 km resolution) is coupled with the boundary layer ozone concentrations. This may be quantified using the ratio of the AOT40 for the full daylight period, and the AOT40 for the period of the day with a well mixed boundary layer from which the base map was interpolated. This ratio, when plotted against altitude is approximately linear (Figure 3.21b), with the largest ratio at high altitude sites (sites which have the smallest diurnal range in concentration). A map of mean altitude for each 1 km x 1 km grid square

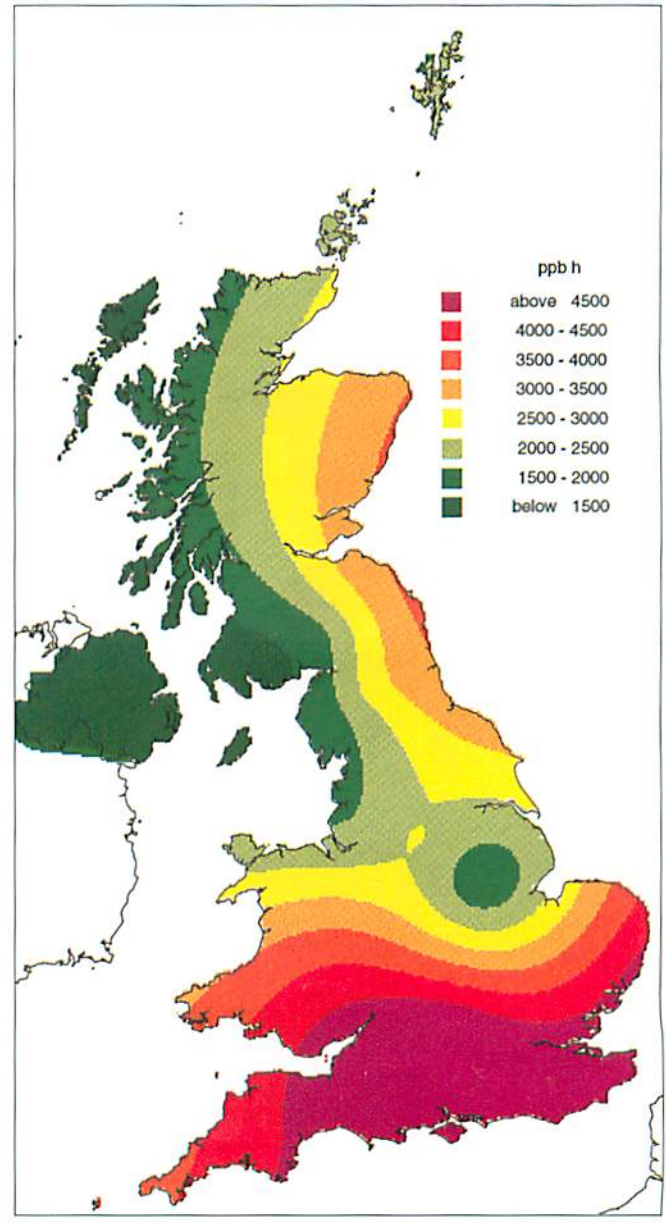


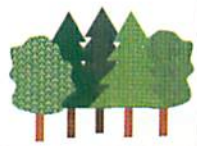
Figure 3.25 AOT40 during 1200-1800 hours for the period May-July, based on 1990 - 94 averaged data.

then enables the relationship from Figure 3.21b to be used to construct an AOT40 map for the entire country (Figure 3.26). The areas exceeding the AOT40 include most of the wheat growing areas in southern and central England but also areas of the uplands and the north where wheat is not grown. The associated paper by Brown *et al* (1995) considers the exceedances in more detail.

AOT40 for forest

The AOT40 for forest is based on daylight hours ozone exposure for the period April to September. The recent change from using 24 hours to daylight hours only at the Kuopio ozone workshop (Karenlampi & Skarby, 1996) is discussed in Chapter 7.1. Adopting a similar procedure to provide a map of regional ozone exposure for forest for the 1200-1800 period, the AOT40 for each of the rural ozone monitoring sites for the 6 summer months (April - September) for the well-mixed atmosphere 1200-1800 GMT, was constructed (Figure 3.27). The relationship between the ratio of AOT40 for the daylight hours to that for the period 1200-1800 (Figure 3.21c) then allows the 1 km x 1 km resolution map of AOT40 for forest to be constructed (Figure 3.28).

Table 3.4 Definition of AOT40 critical levels for crops, semi-natural vegetation and forests (Karenlampi & Skarby, 1996).

Crops (wheat) and semi-natural vegetation 	AOT40 from May to July during daylight hours 3000 ppb hours
Forests 	AOT40 from April to September during daylight hours 10,000 ppb hours

Daylight hours have been defined as when solar radiation exceeds 50 Wm^{-2}. However this data is not available for all sites, and so daylight has been redefined as all hours with a solar zenith angle of 85° or less at the half hour, which can be calculated from the site's latitude and longitude.

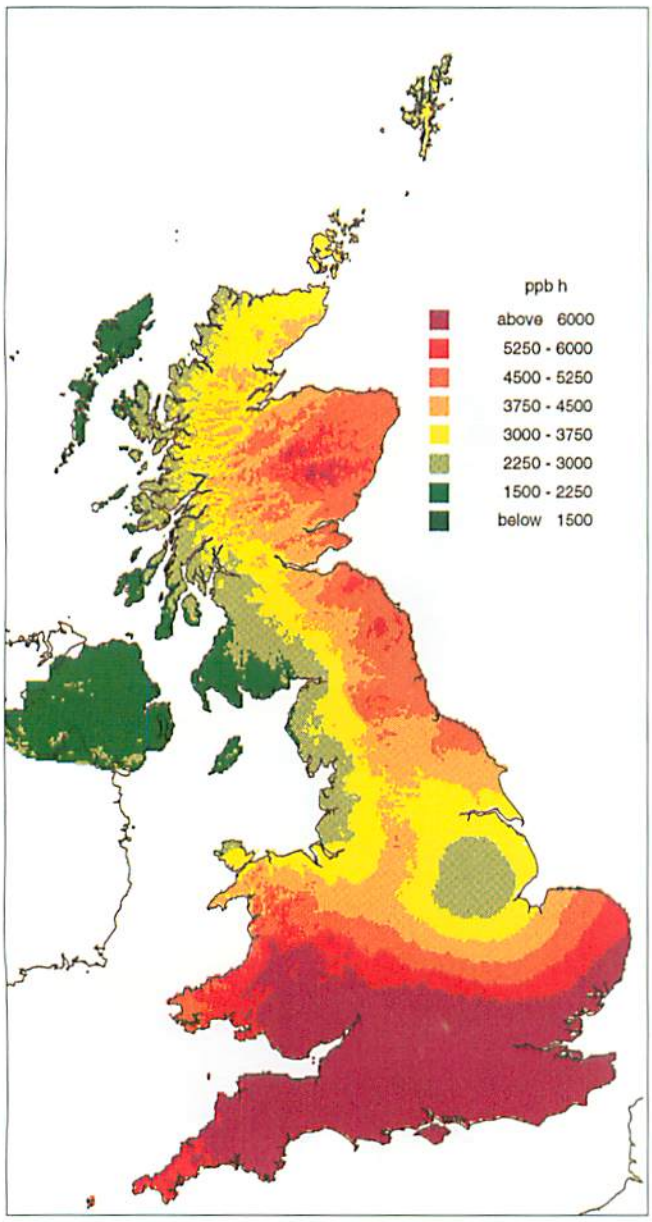


Figure 3.26 AOT40 for wheat during daylight hours for the period May-July, based on 1990 - 94 averaged data in Figure 3.25.

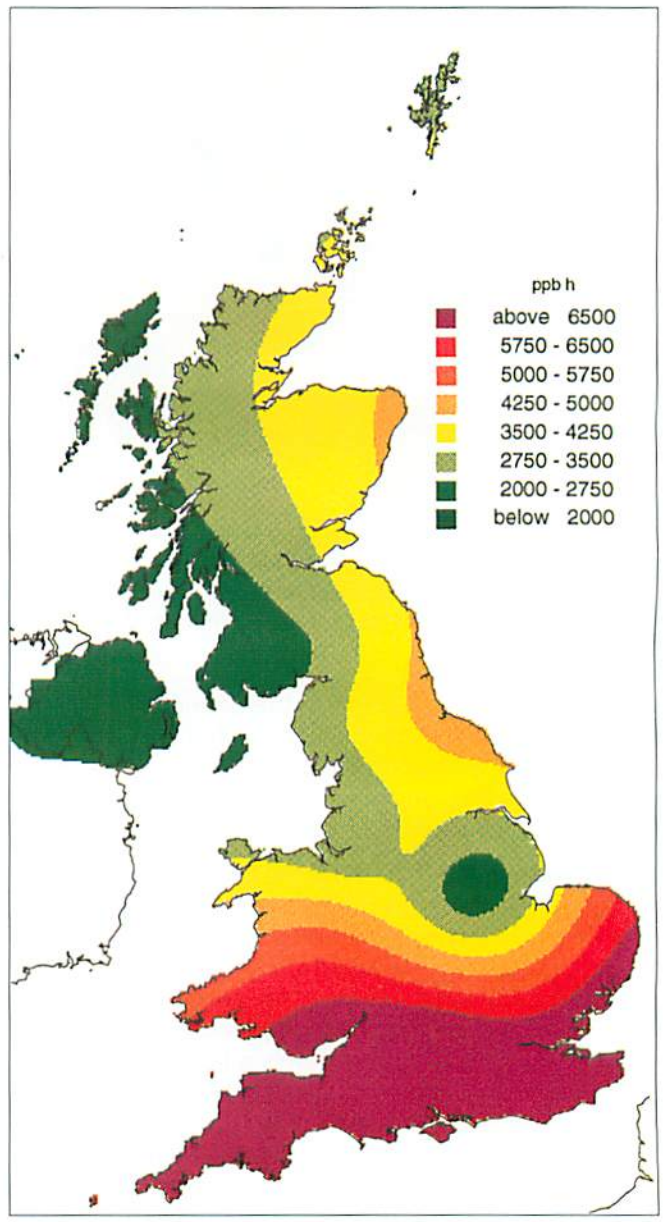


Figure 3.27 AOT40 during 1200-1800 hours for the period April - Sept, based on 1990 - 94 averaged data.

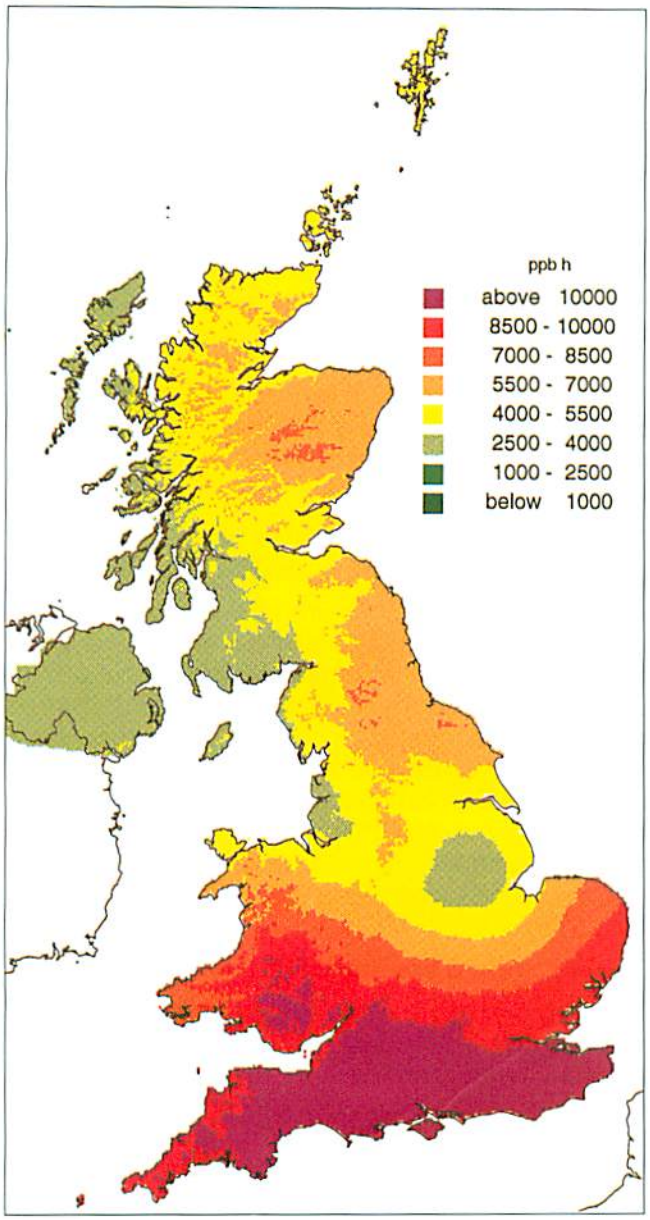


Figure 3.28 AOT40 for forests during daylight hours for the period April - Sept., based on 1990 - 94 averaged data in Figure 3.27.

An urban correction for the AOT40 maps

The same approach for quantifying the urban influence on the summer mean was applied to the AOT40 values. The urban index for the AOT40 crops or forests is defined as :

$$UI = \frac{\text{mapped rural AOT40} - \text{measured urban AOT40}}{\text{mapped rural AOT40}}$$

In this case the urban influence could not be clearly defined as the correlation between UI and the proportion

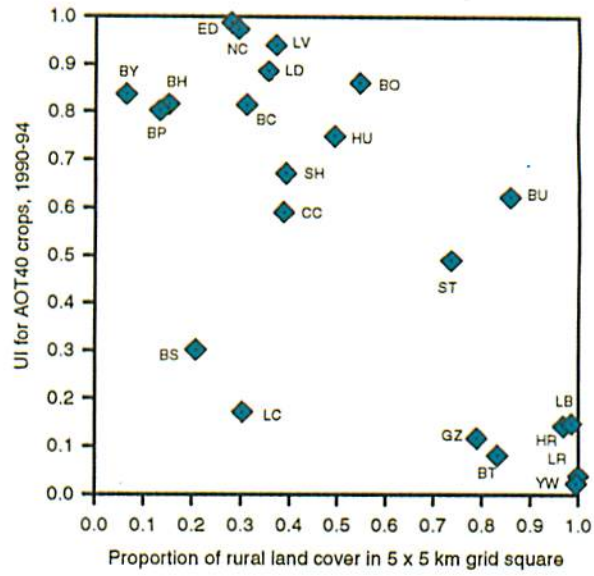


Figure 3.29 Comparison of the urban index for AOT40 crops to the proportion of rural land cover in a 5 x 5 km grid square.

of rural land cover was quite poor, illustrated by Figure 3.29. As the AOT40 is mainly of interest in rural areas an urban correction was not applied.

3.4.3 Mapping the Exceedance of the EPAQS Standard for Ozone

The Expert Panel on Air Quality Standards (EPAQS) has recommended an 8-hour running mean of 50 ppb as an air quality standard for the UK (EPAQS, 1994) and this has recently been proposed as the standard for ozone by the government in "The United Kingdom Air Quality Strategy" (DoE, 1996). An 8-hour running mean is used as EPAQS concluded that exposures to concentrations of around 100 ppb or more for several hours may lead to respiratory effects in some susceptible people and on warm sunny days concentrations may be raised to this level for several hours (EPAQS, 1994).

In this section the number of days a year on which at least one 8 hour running mean exceeds 50 ppb is examined and mapped to assess the degree of exceedance of the standard in the UK. Appendix 4 shows the annual counts for the rural network sites, Dunslair Heights and a selection of urban sites. As a check for data capture only 8 hour periods with at least four hourly averages were counted. The previous maps depended on the definition of an altitude relationship for the variable being mapped, however as an 8 hour running mean period that exceeds 50 ppb is most likely to occur during the period of peak ozone concentration (i.e. the well-mixed period, 1200 - 1800

Table 3.5 The number of days per year on which the 8 hour running mean ozone concentration exceeds 50 ppb, at Wharleycroft and Great Dun Fell, sites separated by 10 km in the horizontal and about 600 m in the vertical.

	TYPE	EAST, km	NORTH, km	ALTITUDE,m	1990	1991	1992	1993	1994	1995	Mean
Wharleycroft, WC	R	369.8	524.7	206	21	37	26	17	18	38	26.2
Great Dun Fell,GD	RR	371.1	532.2	847	30	24	41	15	24	28	27
				Ratio GD/WC	1.43	0.65	1.58	0.88	1.33	0.74	1.03

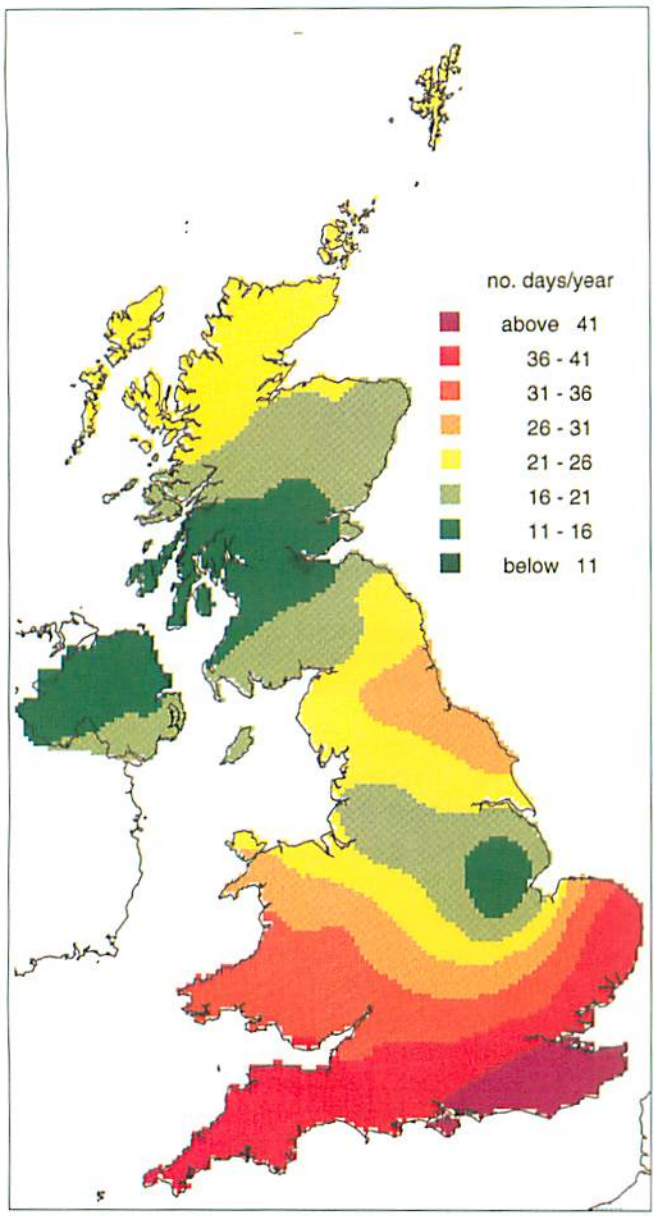


Figure 3.30 The average number of days per year on which the 8 hour running mean exceeded 50 ppb, derived using the average for 1990-95 at rural sites.

hours), the number of days in a year on which an 8 hour running mean exceeds 50 ppb shows very little altitude dependence, see Table 3.5. If well-mixed 8 hour running mean periods are defined as those with at least four hours within the period 1200 - 1800 hours it was found that *ca* 90% of daily maxima exceeding 50 ppb fell within this period. A map can therefore be generated by a simple interpolation from all 17 rural sites, Figure 3.30.

As the 8 hour running mean has been defined to protect human health the next step is to account for urban areas in the map, this was done using the same procedure as before. An urban index for the number of days on which the 8 hour running mean exceeds 50 ppb is defined as equation [viii] below.

$$UI = \frac{\text{mapped rural value} - \text{measured value}}{\text{mapped rural value}} \quad \text{[viii]}$$

This urban index is then related to the proportion of rural land cover in each 5 km grid square (*rurlc*), Figure 3.31, to give the following relationship, [ix].

$$UI = 1.1 - 1.1rurlc,\ r^2 = 0.88 \quad \text{[ix]}$$

The resulting map produced when this equation was applied to the map in Figure 3.30 is shown in Figure 3.32.

The standard for ozone recommended in the 'The UK National Air Quality Strategy' (DoE, 1996) is an eight hour running mean of 50 ppb measured as the 97th percentile. This implies that the number of days on which the 8 hour running mean exceeds 50 ppb should be no more than *ca* 11 days a year to achieve the standard. The map derived here (Figure 3.32) shows that this standard is currently exceeded in most of the UK (98%) with the exception of some city centres and the central region of Scotland.

3.4.4 Accuracy and Uncertainties in the Maps

As has been described ozone concentrations can vary considerably across urban, suburban, rural and upland areas. The maps presented here give a broad picture of ozone in the UK and incorporate our current understanding of the processes which influence surface ozone concentrations. However, the values in an individual grid square should not be interpreted literally; they are the best estimates and while well supported by the available data, these data are only available at a limited number of rural and urban sites and the mapped ozone exposure may differ from the actual value by a substantial factor.

The influence of site choice on interpolation results

The network of rural monitoring stations provides spatial patterns in mean ozone concentration and exceedance of thresholds. However, with individual stations in many areas separated by 100 km or more the interpolations on maps over large areas are very sensitive to local site factors. An example is a large

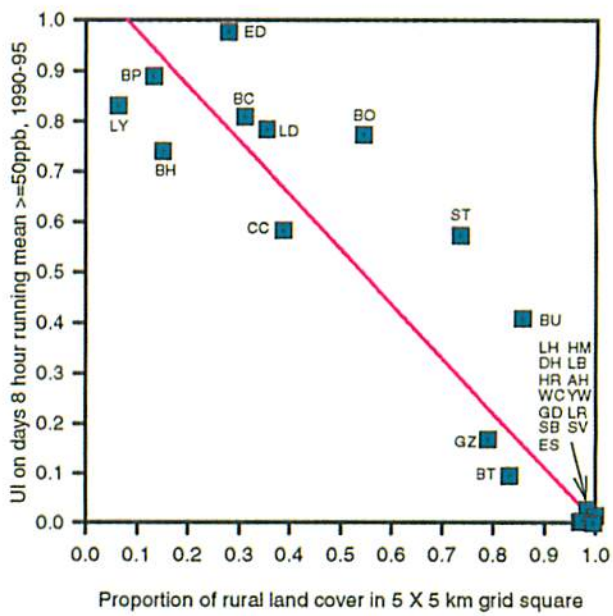


Figure 3.31 Comparison of the urban index for the number of days per year on which the 8 hour running mean exceeds 50 ppb to the proportion of rural land cover in a 5 x 5 km grid square.

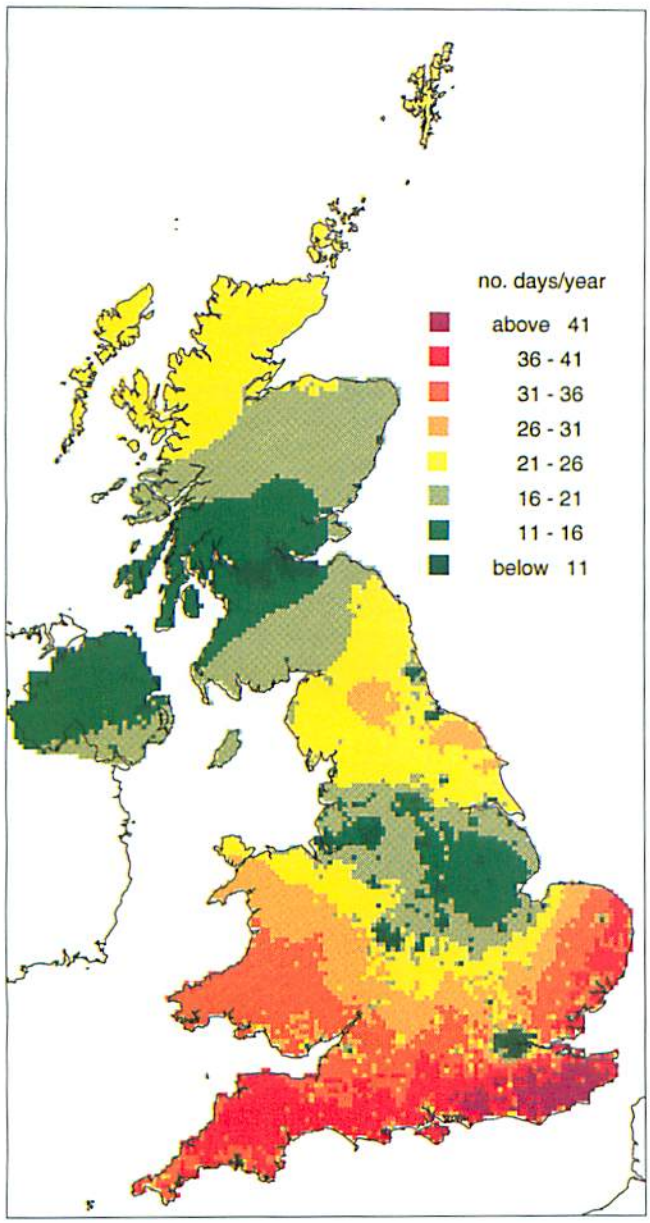


Figure 3.32 The 1990-95 average number of days per year on which the 8 hour running mean exceeded 50 ppb, compensated for the effects of urban areas.

area of the East Midlands of England which shows low mean ozone concentrations and low AOT40 exposure (e.g. Figs. 3.20, 3.25, 3.27). This effect results from the low ozone concentrations at Bottesford, in the Trent Valley relatively close to major roads and urban areas. The mapping interpolation indicates a large area of low ozone exposure (150 km in diameter) extending to the Wash and to the Lincolnshire Wolds. In practice the ozone concentrations in remote Lincolnshire may be substantially larger but there are insufficient monitoring sites to check the interpolation. Similarly, data for Glazebury generate a zone of relatively low ozone exposure in rural N. Wales and data for Bush may generate low levels in the highlands of Scotland. The south coast site at Lullington Heath generates large concentrations of ozone over extensive areas of SE England when in practice the inland sheltered areas may experience substantially lower exposures. These problems can be solved by a large expansion of the network. However, further detailed analysis of individual site data and studies of the influence of local site factors on the ozone climatology at particular locations may provide a more rigorous methodology to interpolate ozone exposure over the UK landscape.

3.5 Trends in Ozone Concentration

3.5.1 Changes with time in Average Concentrations

The annual mean ozone concentrations in Europe are currently about a factor of 2 larger than those during the latter part of the last century (Voltz & Kley, 1988; Anfossi *et al*, 1991). The increase in mean ozone concentration seems to have been since 1940. A brief analysis is given in Chapter 8; for a more detailed description see the last PORG Report (PORG, 1993).

The UK ozone monitoring network data which provide broad countryside coverage from 1987 onwards showed an increase in annual mean ozone concentrations at rural sites over the short period 1986-1991, and a decrease in annual mean ozone concentration at urban sites (Dollard *et al* 1995). The trends were of the order +1 ppb y^{-1} at the rural sites and -0.5 ppb y^{-1} at urban sites. These data covered a very short period and inter-year variability in meteorological conditions cause variations in mean ozone concentrations at all sites which are much larger (typically 1-5 ppb) than the magnitude of the observed short-term trends (0.1 - 1.0 ppb). The decrease in urban ozone concentrations during the late 1980s is broadly consistent with the growth in vehicular traffic and their NO emissions. Increases in rural ozone concentration of about 1 ppb y^{-1} have also been reported for the summit of Zugspitze (2964 m asl, close to the German/Austrian border) for the period 1978 to 1990 (Seiler *et al*, 1991). However, the data show much smaller changes in the latter years of the monitoring period.

An analysis of the trends in ozone concentrations for the UK sites for the entire record (1972 - 1995), and a detailed examination of the period 1986 - 1995, is therefore an important part of the assessment of the ozone climate over the UK. The tabulated analysis of trends at all rural UK ozone monitoring stations and selected urban sites is provided as Table 3.6. The table includes an analysis of the trends in annual mean concentrations, summer (April - September inclusive), winter (October - March inclusive), the AOT40 Forest, AOT40 Wheat and the number of days a year on which an 8 hour running mean exceeds 50 ppb. The probability value given on the table indicates the statistical validity of the trend; only if the probability is no more than 0.05 can it be assumed that concentrations at the site have increased or decreased.

These data show either no change or a small upward trend in annual mean ozone concentration, averaging +0.5 ppb y^{-1} at most (14 out of 16) of the rural sites. The trend is significantly positive (at the 5% level) at 9 of the rural sites. At the sites which are appreciably influenced by local sources of NO_x including Stevenage, London, Glazebury, and Bottesford, the trend is negative but much more variable averaging -0.3 ppb y^{-1}.

These trends, both positive and negative, are all small relative to the inter-year variability in ozone concentration at individual sites. The trend is also largely driven by the first 2 years of the record, 1987 and 1988, for which the annual means were low relative to the period 1989 to 1995. The overall pattern of change averaged for all sites in the network is illustrated in Figure 3.33 which shows an increase after 1986, when the number of sites reached 16 and was representative of rural areas for the entire country. Clearly, in the absence of the relatively low ozone years of 1987 and 1988, there is little or no change in ozone concentration overall.

The inter-year variability for the exceedances over thresholds, AOT40 Forest and Wheat, are also very large, obscuring any long term trends throughout the country. In a statistical sense there are no long-term trends in these values discernible within the data set.

Table 3.6 Trends in several variables at sites with more than six years of data with data capture ≥ 60%

Site Ref	Variable	Period	No. of Years	Trend	Std Error	Probability
Strath Vaich	Annual mean	1987 - 95	9	0.42	0.16	0.032
	Annual mean	1988 - 95	8	0.29	0.18	0.153
	Winter mean	1987 - 95	9	0.63	0.32	0.088
	Winter mean	1988 - 95	8	0.37	0.36	0.34
	Summer mean	1987 - 95	9	0.31	0.19	0.146
	Summer mean	1988 - 95	8	0.22	0.24	0.391
	AOT40 forest	1987 - 95	9	198	211	0.379
	AOT40 wheat	1987 - 95	9	107	200	0.609
	Days year 8h.r.m >= 50ppb	1987 - 95	9	1.37	1.26	0.314
	Days year 8h.r.m >= 50ppb	1988 - 95	8	0.69	1.54	0.671
Bush	Annual mean	1986 - 95	10	0.22	0.18	0.272
	Annual mean	1988 - 95	8	-0.03	0.22	0.894
	Winter mean	1986 - 95	10	0.23	0.28	0.434
	Winter mean	1988 - 95	8	-0.06	0.31	0.853
	Summer mean	1986 - 95	10	0.24	0.15	0.163
	Summer mean	1988 - 95	8	0.03	0.22	0.905
	AOT40 forest	1986 - 95	10	-48	140	0.742
	AOT40 wheat	1986 - 95	10	-18	115	0.882
	Days year 8h.r.m >= 50ppb	1986 - 95	10	-0.55	0.7	0.459
	Days year 8h.r.m >= 50ppb	1988 - 95	8	-1.77	0.86	0.085
Eskdalemuir	Annual mean	1986 - 95	10	0.59	0.24	0.04
	Annual mean	1988 - 95	8	0.02	0.19	0.937
	Winter mean	1986 - 95	10	0.58	0.28	0.073
	Winter mean	1988 - 95	8	-0.03	0.27	0.907
	Summer mean	1986 - 95	10	0.66	0.25	0.032
	Summer mean	1988 - 95	8	0.07	0.22	0.776
	AOT40 forest	1986 - 95	10	190	147	0.234
	AOT40 wheat	1986 - 95	10	140	132	0.321
	Days year 8h.r.m >= 50ppb	1986 - 95	10	0.91	0.71	0.236
	Days year 8h.r.m >= 50ppb	1988 - 95	8	-0.24	0.93	0.807
Lough Navar	Annual mean	1987 - 95	9	0.15	0.15	0.357
	Annual mean	1988 - 95	8	-0.03	0.14	0.861
	Winter mean	1987 - 95	9	0.42	0.26	0.15
	Winter mean	1988 - 95	8	0.14	0.26	0.618
	Summer mean	1987 - 95	9	-0.01	0.16	0.938
	Summer mean	1988 - 95	8	-0.17	0.17	0.371
	AOT40 forest	1987 - 95	9	-133	140	0.374
	AOT40 wheat	1987 - 95	9	-85	145	0.575
	Days year 8h.r.m >= 50ppb	1987 - 95	9	-0.07	0.72	0.929
	Days year 8h.r.m >= 50ppb	1988 - 95	8	-0.51	0.87	0.576
Great Dun Fell	Annual mean	1986 - 95	10	0.71	0.24	0.02
	Annual mean	1988 - 95	8	0.22	0.15	0.182
	Winter mean	1986 - 95	10	0.81	0.31	0.03
	Winter mean	1988 - 95	8	0.36	0.38	0.384
	Summer mean	1986 - 95	10	0.69	0.28	0.041
	Summer mean	1988 - 95	8	0.17	0.22	0.469
	AOT40 forest	1987 - 95	9	-108	274	0.704
	AOT40 wheat	1987 - 95	9	2	307	0.995
	Days year 8h.r.m >= 50ppb	1987 - 95	9	-0.12	1.05	0.915
	Days year 8h.r.m >= 50ppb	1988 - 95	8	-1.02	1.18	0.418
Wharleycroft	Annual mean	1985 - 95	11	0.3	0.71	0.688
	Annual mean	1986 - 95	10	1.46	0.29	0.001
	Annual mean	1988 - 95	8	0.77	0.24	0.018
	Winter mean	1986 - 95	10	1.45	0.27	0.001
	Winter mean	1988 - 95	8	0.75	0.15	0.002
	Summer mean	1985 - 95	11	0.3	0.61	0.637
	Summer mean	1986 - 95	10	1.24	0.33	0.005
	Summer mean	1988 - 95	8	0.72	0.39	0.113
	AOT40 forest	1987 - 95	9	397	220	0.114
	AOT40 wheat	1987 - 95	8	238	112	0.079
	Days year 8h.r.m >= 50ppb	1987 - 95	9	2.27	1.13	0.086
	Days year 8h.r.m >= 50ppb	1988 - 95	8	1.52	1.35	0.304

Site Ref	Variable	Period	No. of Years	Trend	Std Error	Probability
High Muffles	Annual mean	1987 - 95	9	1	0.28	0.009
	Annual mean	1988 - 95	8	0.56	0.15	0.009
	Winter mean	1987 - 95	9	0.78	0.21	0.008
	Winter mean	1988 - 95	8	0.61	0.24	0.045
	Summer mean	1987 - 95	9	1.08	0.47	0.055
	Summer mean	1987 - 95	9	1.08	0.47	0.055
	Summer mean	1988 - 95	8	0.35	0.26	0.237
	AOT40 forest	1988 - 95	8	85	203	0.69
	AOT40 wheat	1988 - 95	8	-14	243	0.956
	Days year 8h.r.m >= 50ppb	1988 - 95	8	0.32	0.89	0.732
	Days year 8h.r.m >= 50ppb	1988 - 95	8	0.32	0.89	0.732
Mace Head	Annual mean	1987 - 95	9	0.67	0.29	0.053
	Annual mean	1988 - 95	8	0.19	0.12	0.145
	Winter mean	1987 - 95	9	0.72	0.31	0.054
	Winter mean	1988 - 95	8	0.23	0.18	0.23
	Summer mean	1987 - 95	9	0.65	0.32	0.085
	Summer mean	1988 - 95	8	0.15	0.19	0.458
	AOT40 forest	1987 - 95	9	348	167	0.075
	AOT40 wheat	1987 - 95	9	92	110	0.431
	Days year 8h.r.m >= 50ppb	1987 - 95	9	1.85	1.66	0.301
	Days year 8h.r.m >= 50ppb	1988 - 95	8	0.96	2.03	0.652
Glazebury	Annual mean	1989 - 95	7	-0.1	0.2	0.653
	Winter mean	1989 - 95	7	-0.08	0.26	0.766
	Summer mean	1989 - 95	7	-0.16	0.25	0.554
	AOT40 forest	1989 - 95	7	-109	197	0.602
	AOT40 wheat	1989 - 95	7	-92	221	0.695
	Days year 8h.r.m >= 50ppb	1989 - 95	7	0.18	1.05	0.872
Ladybower	Annual mean	1988 - 95	8	0.27	0.25	0.31
	Winter mean	1988 - 95	8	0.26	0.18	0.202
	Summer mean	1988 - 95	8	0.44	0.33	0.228
	AOT40 forest	1989 - 95	6	-356	352	0.37
	AOT40 wheat	1989 - 95	6	-252	260	0.386
	Days year 8h.r.m >= 50ppb	1989 - 95	5	-2.1	1.29	0.201
Bottesford	Annual mean	1981 - 95	15	-0.37	0.16	0.041
	Annual mean	1986 - 95	10	-0.23	0.35	0.527
	Annual mean	1988 - 95	8	0.34	0.43	0.451
	Winter mean	1981 - 95	15	-0.12	0.16	0.457
	Winter mean	1986 - 95	10	-0.16	0.34	0.66
	Winter mean	1988 - 95	8	0.46	0.36	0.246
	Summer mean	1981 - 95	14	-0.45	0.18	0.028
	Summer mean	1986 - 95	9	-0.15	0.34	0.673
	Summer mean	1988 - 95	7	0.37	0.39	0.385
	AOT40 forest	1981 - 95	14	-272	132	0.061
	AOT40 wheat	1981 - 95	14	-126	80	0.142
	Days year 8h.r.m >= 50ppb	1981 - 95	14	-1.56	0.72	0.052
	Days year 8h.r.m >= 50ppb	1986 - 95	9	-0.22	0.94	0.82
	Days year 8h.r.m >= 50ppb	1988 - 95	7	0.87	1.34	0.545
Aston Hill	Annual mean	1986 - 95	10	0.65	0.25	0.031
	Annual mean	1988 - 95	8	0.12	0.25	0.642
	Winter mean	1986 - 95	10	0.6	0.31	0.087
	Winter mean	1988 - 95	8	0.1	0.32	0.773
	Summer mean	1986 - 95	10	0.8	0.29	0.025
	Summer mean	1988 - 95	8	0.11	0.23	0.661
	AOT40 forest	1987 - 95	9	232	298	0.46
	AOT40 wheat	1987 - 95	8	130	248	0.619
	Days year 8h.r.m >= 50ppb	1987 - 95	9	1.23	1.3	0.375
	Days year 8h.r.m >= 50ppb	1988 - 95	8	-0.12	1.35	0.932
Sibton	Annual mean	1973 - 95	22	-0.22	0.15	0.158
	Annual mean	1987 - 95	9	0.43	0.17	0.035
	Annual mean	1988 - 95	8	0.22	0.15	0.18
	Winter mean	1973 - 95	20	0	0.15	0.974
	Winter mean	1987 - 95	9	0.57	0.17	0.014
	Winter mean	1988 - 95	8	0.39	0.18	0.074
	Summer mean	1973 - 95	22	-0.06	0.15	0.71
	Summer mean	1987 - 95	9	0.44	0.3	0.181
	Summer mean	1988 - 95	8	0.01	0.2	0.979
	AOT40 forest	1975 - 95	16	-126	162	0.449
	AOT40 wheat	1975 - 95	17	-21	110	0.852
	Days year 8h.r.m >= 50ppb	1977 - 95	14	-0.15	0.53	0.779
	Days year 8h.r.m >= 50ppb	1988 - 95	8	0.35	1.03	0.75
Lullington Heath	Annual mean	1986 - 95	10	0.86	0.36	0.043
	Annual mean	1988 - 95	8	0.14	0.38	0.723
	Winter mean	1986 - 95	10	0.55	0.31	0.107
	Winter mean	1988 - 95	8	0.16	0.41	0.706
	Summer mean	1987 - 95	9	0.48	0.39	0.252
	Summer mean	1988 - 95	8	0.06	0.39	0.876

Site Ref	Variable	Period	No. of Years	Trend	Std Error	Probability
Lullington Heath	AOT40 forest	1988 - 95	8	111	570	0.852
	AOT40 wheat	1988 - 95	8	69	446	0.882
	Days year 8h.r.m >= 50ppb	1988 - 95	8	-0.54	2.21	0.817
Yarner Wood	Annual mean	1987 - 95	9	0.45	0.43	0.324
	Annual mean	1988 - 95	8	-0.18	0.29	0.558
	Winter mean	1987 - 95	9	0.18	0.31	0.566
	Winter mean	1988 - 95	8	-0.21	0.27	0.471
	Summer mean	1987 - 95	9	0.72	0.62	0.286
	Summer mean	1988 - 95	8	-0.16	0.46	0.735
	AOT40 forest	1988 - 95	8	-192	672	0.784
	AOT40 wheat	1988 - 95	8	-128	483	0.8
	Days year 8h.r.m >= 50ppb	1988 - 95	8	-0.3	2.39	0.905
Harwell	Annual mean	1976 - 95	14	-2.54	0.73	0.005
	Annual mean	1986 - 95	10	0.43	0.15	0.023
	Annual mean	1988 - 95	8	0.41	0.21	0.102
	Winter mean	1984 - 95	12	-0.02	0.23	0.939
	Winter mean	1986 - 95	10	0.17	0.32	0.604
	Winter mean	1988 - 95	8	0.07	0.48	0.886
	Summer mean	1976 - 95	14	-2.3	0.72	0.008
	Summer mean	1986 - 95	10	0.73	0.22	0.01
	Summer mean	1988 - 95	8	0.89	0.33	0.036
	AOT40 forest	1983 - 95	13	170	199	0.411
	AOT40 wheat	1983 - 95	13	257	122	0.058
	Days year 8h.r.m >= 50ppb	1984 - 95	12	0.76	1.18	0.537
	Days year 8h.r.m >= 50ppb	1986 - 95	10	2.92	1.28	0.051
	Days year 8h.r.m >= 50ppb	1988 - 95	8	2.19	2	0.316
Stevenage	Annual mean	1976 - 94	19	-0.89	0.49	0.083
	Annual mean	1986 - 94	9	0.59	0.18	0.013
	Annual mean	1988 - 94	7	0.71	0.21	0.019
	Winter mean	1977 - 94	18	0	0.13	0.988
	Winter mean	1986 - 94	9	0.63	0.27	0.053
	Winter mean	1988 - 94	7	0.82	0.36	0.072
	Summer mean	1976 - 94	19	-0.81	0.47	0.105
	Summer mean	1986 - 94	9	0.8	0.17	0.003
	Summer mean	1988 - 94	7	0.94	0.24	0.011
	AOT40 forest	1977 - 93	17	-87	190	0.653
	AOT40 wheat	1977 - 93	16	-32	132	0.813
	Days year 8h.r.m >= 50ppb	1977 - 93	16	-0.44	0.7	0.537
	Days year 8h.r.m >= 50ppb	1987 - 93	7	0.82	1.13	0.499
	Days year 8h.r.m >= 50ppb	1988 - 93	6	0.74	1.59	0.665
Central London and Bridge Place	Annual mean	1972 - 95	23	-0.12	0.08	0.15
	Annual mean	1986 - 95	9	0.44	0.22	0.083
	Annual mean	1988 - 95	7	0.45	0.18	0.06
	Winter mean	1972 - 95	23	0.08	0.07	0.294
	Winter mean	1986 - 95	9	0.53	0.16	0.014
	Winter mean	1988 - 95	7	0.62	0.06	0
	Summer mean	1972 - 95	23	-0.34	0.13	0.015
	Summer mean	1986 - 95	9	0.49	0.3	0.147
	Summer mean	1988 - 95	7	0.43	0.27	0.172
	AOT40 forest	1973 - 94	18	-289	86	0.004
	AOT40 wheat	1973 - 95	20	-165	44	0.002
	Days year 8h.r.m >= 50ppb	1973 - 95	17	-1.18	0.36	0.005
	Days year 8h.r.m >= 50ppb	1986 - 95	8	-0.61	0.77	0.458
	Days year 8h.r.m >= 50ppb	1988 - 95	7	-0.23	1.04	0.832

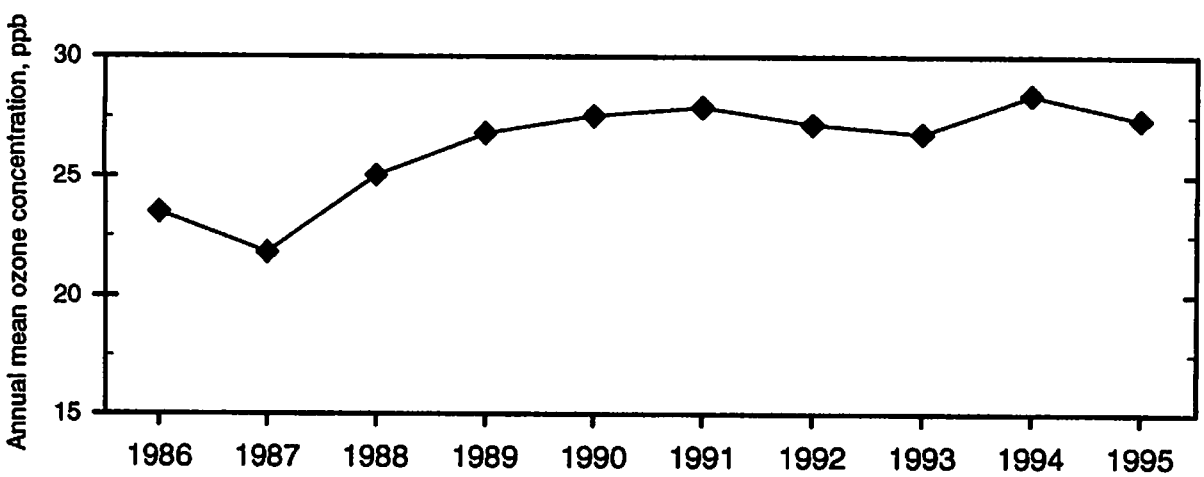


Figure 3.33 Annual average of all rural network sites ozone concentrations from 1986 to 1995.

3.5.2 Changes with Time in Peak Concentrations

The short record of ozone monitoring by an adequate rural network (1986-1995) combined with large inter-annual variability make it difficult to discern clear regional trends. The data show a small increase in ozone during the early years 1986-1989 and little or no change at the remote rural stations since then.

The sites at which substantial (> 5 ppb) concentrations of NO_2 are present are clearly influenced by local largely vehicular sources of NO_x. At these sites the ozone concentrations have, in general, decreased since 1987. There are, however, other features of the data which indicate that appreciable changes have taken place in the ozone climate of the UK.

The early ozone measurements (1972-1985) show hourly average concentrations reaching and exceeding 200 ppb, Table 3.7. In particular, in the hot summer of 1976, ozone concentrations at Harwell exceeded 250 ppb (this value is not given in Table 3.7 as data capture for this year was less than 60%), and yet the recent hot summer of 1995 produced relatively modest concentrations of 90 to 130 ppb. These high values (>150 ppb O_3) were not uncommon during the first decade of ozone monitoring in the UK, even though measurements were only available at a few sites. Taking the hourly maximum ozone concentrations observed at any site for each month of the year and plotting these for the period 1972 to 1985 shows that there were about 20 occasions during May - August on which peak concentrations exceeded 150 ppb, and the average June maximum was 140 ppb (Figure 3.34a).

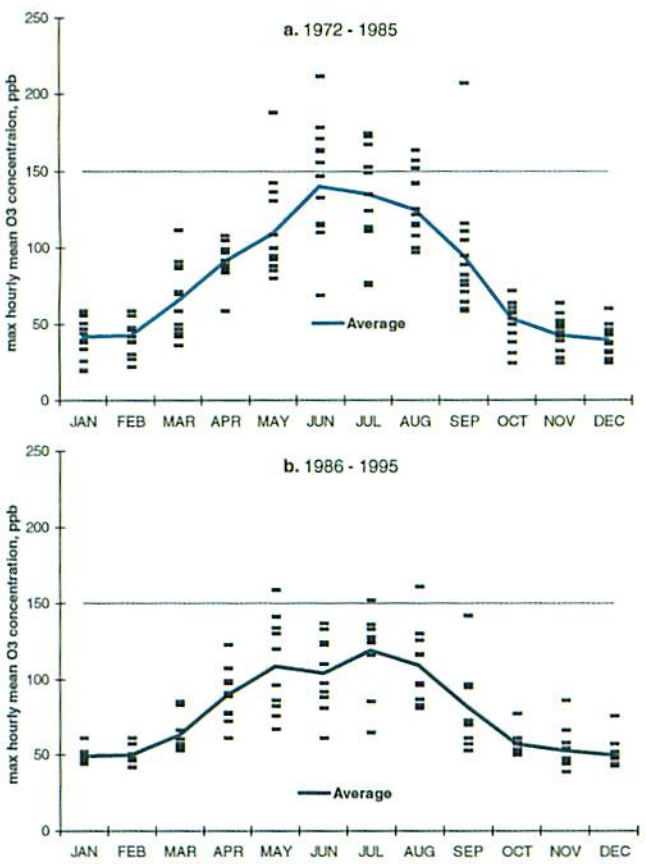


Figure 3.34 Maximum hourly concentration observed at any site during each month of years a.1972-1985 and b.1986-1995.

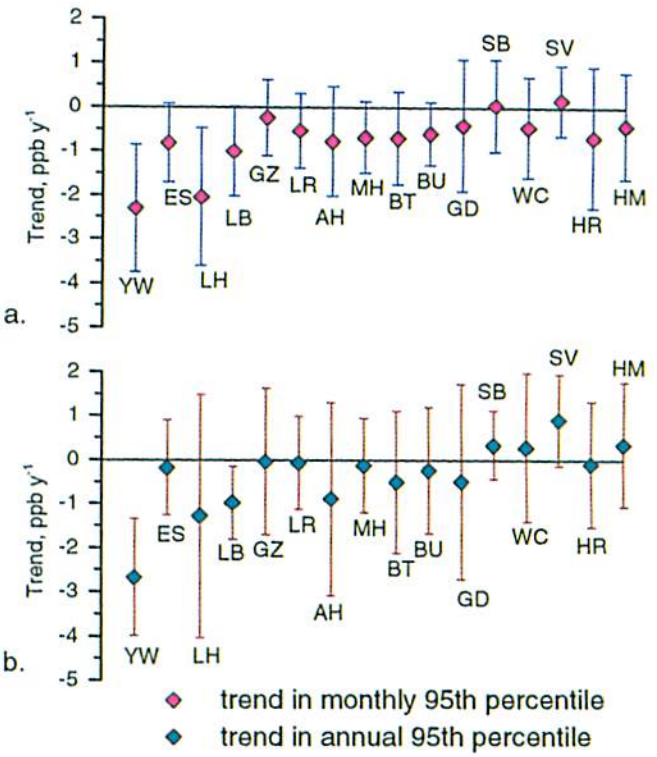


Figure 3.35 Trends in monthly and annual 95th percentiles for 1989 to 1994 as ppb y^{-1}.

For the subsequent period 1986-1995, the maximum only exceeded 150 ppb three times and then only just, and the mean maximum over the 10 years in July was 119 ppb (Figure 3.34b). There appears therefore to be clear evidence of a reduction in the magnitude of the maximum values occurring during summer photochemical oxidant episodes. These observations are consistent with those elsewhere in Europe (see Chapter 8).

A decline in peak concentrations was also found over the short period 1989 to 1994. Annual trends in the monthly 95th percentile ozone concentrations were calculated by fitting a linear trend combined with a series of 12 parameters that model the monthly variations. Out of 16 rural sites, 14 show a negative trend of between -0.2 ppb y^{-1} and -2.3 ppb y^{-1}, with an average of -0.8 ppb y^{-1}, see Figure 3.35a. Fitting the monthly values significantly reduces the uncertainty in the trend as can be seen when a straight line is fitted to the yearly 95th percentiles, Figure 3.35b. However these values also show a negative trend at most sites.

3.5.3 Influences on Trends in Ozone Concentration

There are many factors that may influence long term ozone concentrations, complicating the analysis and interpretation of trends in ozone. The main influences on trends in the UK are: variation in the Northern hemisphere background concentration; changes in emissions of precursor concentrations from Europe and the UK; changes in the annual pattern of meteorological conditions across Europe and the UK.

The following detailed scrutiny of the Mace Head monitoring data, over the period 1990 - 96 inclusive, and a comparison of the summers of 1976 and 1995, show the influence of some of these factors.

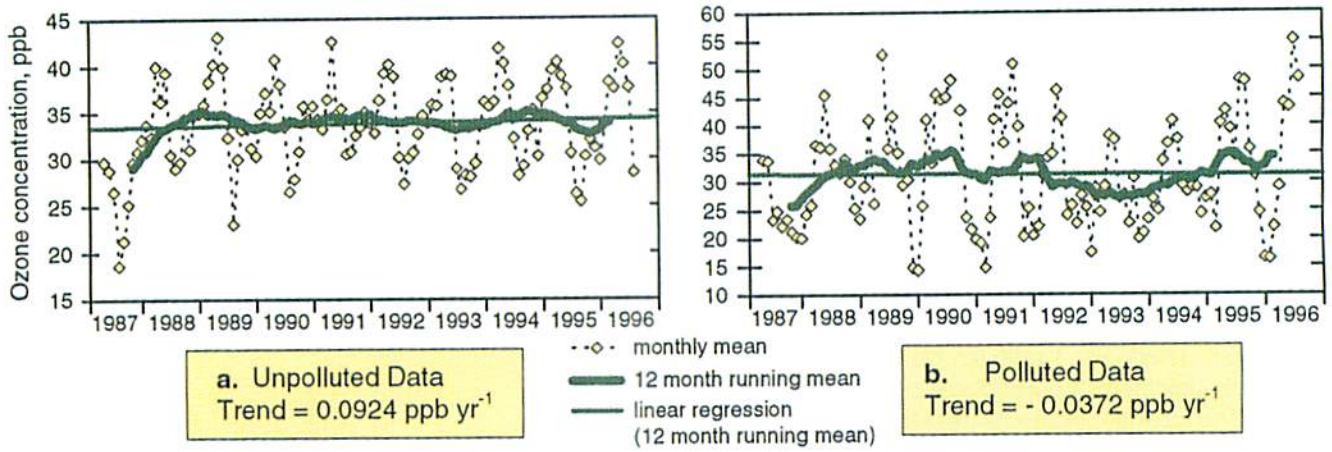


Figure 3.36 Monthly mean and 12 month running mean ozone concentrations at Mace Head with a linear regression on the 12 month running mean, in (a) unpolluted air masses and (b) polluted air masses.

Analysis of trends at Mace Head

Isentropic back track trajectory analyses, EMEP daily sector allocations and simultaneous halocarbon measurements provide three independent and unambiguous methods of allocating air mass origins to each hourly mean measurement. Thus, trends in ozone concentration in air masses described as either "northern hemisphere background" or "European" can be calculated.

During the period 1990-1994, 61% of the hourly ozone measurements made at Mace Head were allocated to the background sector. The mean ozone concentration reported for these measurements was 34.9 ± 4.3 ppb and a significant downwards trend of -0.046 ± 0.03 ppb per month or -1.6% per year was apparent over this period.

Looking over the entire 1987 - 1996 period, Figure 3.36a shows the record of the monthly mean concentrations for unpolluted or background air masses. It appears that background ozone concentrations, having declined over the 1990-1994 period, recovered during the 1995-1996 period. Over the 1990-1996 period, there has been an upwards trend of +0.092 ppb per year or +0.2% per year.

These changes in background ozone should be seen in the light of the global measurements of ozone and of the other major tropospheric trace gases. During the

Maximum	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
1972							111	126	79		24	24
1973	20	27	50	92	100	115	113	142	116	31	42	43
1974	44	46	71	84	109	163	76	97	65	38	43	32
1975	19	22	88	108	93	171	173	157	95	24	28	27
1976	40	38	47	99	188	212	175	152	105	50	48	31
1977	34	39	112	59	143	179	135	100	71	64	64	50
1978	56	56	70	89	131	147	149	100	82	72	52	37
1979	38	48	44	89	93	156	153	108	89	57	32	46
1980	57	30	42	108	95	110	77	116	76	44	27	26
1981	26	27	36	97	85	69	114	164	207	54	45	45
1982	51	46	91	105	137	164	124	122	111	58	57	60
1983	59	59	59	87	80	116	168	115	59	54	50	43
1984	47	42	87	85	88	133	174	143	60	61	39	38
1985	50	72	56	83	79	88	149	111	114	88	46	59
Average	**42**	**42**	**66**	**91**	**109**	**140**	**135**	**125**	**95**	**53**	**43**	**40**
1986	51	47	66	78	82	137	128	83	73	61	66	57
1987	48	42	57	99	159	81	133	126	57	53	58	52
1988	61	61	85	123	86	92	65	116	95	51	44	43
1989	44	51	60	89	130	124	136	117	95	57	45	44
1990	49	57	83	98	120	88	152	161	142	61	48	44
1991	46	47	56	77	67	61	126	96	97	77	86	76
1992	49	51	53	91	141	123	116	98	70	54	45	44
1993	46	46	55	107	96	133	85	81	72	50	55	48
1994	52	47	60	72	76	98	127	87	61	52	39	49
1995	48	48	56	61	134	110	124	130	53	58	44	44
Average	**49**	**50**	**63**	**90**	**109**	**105**	**119**	**110**	**82**	**57**	**53**	**50**

Table 3.7 Maximum hourly average recorded in each year, from all sites with annual data capture ≥ 60%.

1990-1994 period, the upwards trends in carbon dioxide, methane and nitrous oxide noted during the 1980's all slowed dramatically. These dramatic changes in trends have not been quantitatively accounted for, although they have been tentatively explained as a Mount Pinatubo effect (erupted in 1991). Here we see evidence of a corresponding impact on ozone. Subsequently, during 1994 and 1995, the upwards trends in all these tropospheric trace gases found during the 1980's have resumed, ozone included.

During the 1990-1994 period, European air masses flowing out into the North Atlantic region over Mace Head showed a mean ozone concentration of 32.5 ± 4.5 ppb and a downwards trend of -0.12 ± 0.08 ppb per month or 4.6% per year.

Figure 3.36b shows the trends in the monthly mean ozone concentrations in polluted air masses over the entire 1987 - 1996 period. The overall trend is downwards but with a much reduced trend of -0.0031 ppb per month or -1.3% per year. The marked downwards trend in the mean ozone concentrations observed for European air masses during 1992-1994 has almost completely been made up during 1995 and 1996. The behaviour of ozone here appears to be following the broad scale meteorological patterns, with relatively poor summers giving low summertime ozone levels at Mace Head and the warmer summers in 1995 and 1996 giving somewhat higher mean ozone concentrations.

Concentrations of methane and nitrous oxide in European air masses follow a similar pattern to ozone, supporting the conclusion that currently meteorology is having the largest influence on trends in Europe. Reductions in precursor emissions from some European countries, however, will have reduced the potential for ozone formation.

Comparison of the summers of 1976 and 1995

The exceptionally hot, dry and sunny weather during the summer of 1995 led to an expectation of peaks in ozone concentration of similar magnitude to those that occurred during the summer of 1976, when the UK also experienced a heat wave. However, concentrations

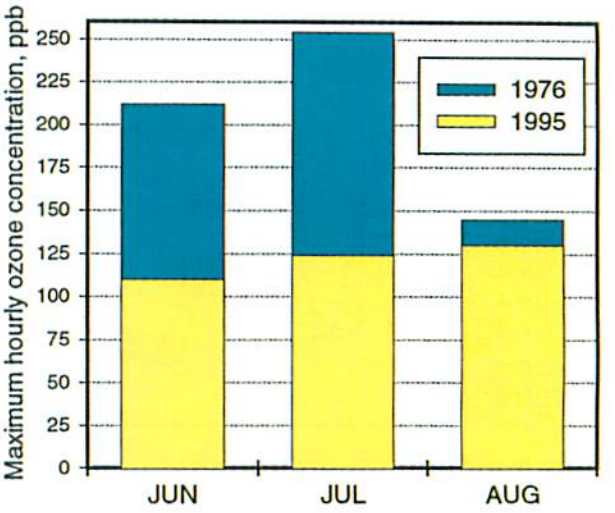


Figure 3.37 Maximum hourly mean O_3 concentrations recorded during the months of June, July and August for 1976 and 1995.

during 1995 never reached the levels of 1976, see Figure 3.37, even though ozone levels were significantly higher than those reported by the rural ozone network in recent years.

In the following discussion, some of the features of the summer months June, July and August of 1976 and 1995 are compared to see if any explanation can be found for the marked differences in the peak ozone concentrations, despite the obvious similarities in weather conditions. Table 3.8 summarises the patterns of weather that occurred over the three months.

Although the amount of ozone monitoring data available for 1976 is limited, two major ozone episodes were measured during 1976, see Figure 3.38:

1. 22nd to 29th June when ozone peaked at 211 ppb at Teddington, Middlesex and 212 ppb in Central London.
2. 3rd to 5th July when the maximum hourly concentration for the year of 254 ppb was recorded at Harwell, Oxfordshire.

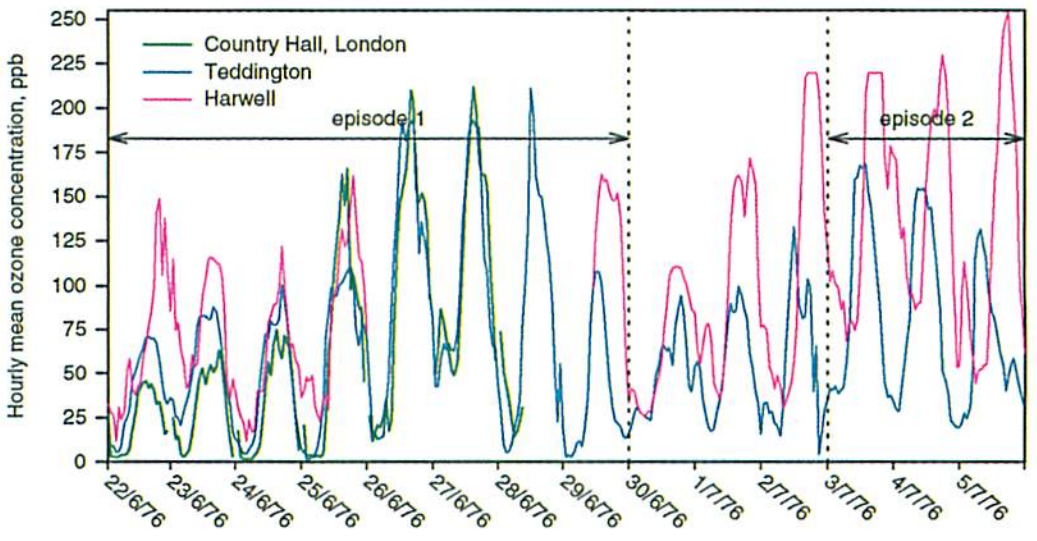


Figure 3.38 Hourly mean ozone concentrations from 22/6/76 to 5/7/76.

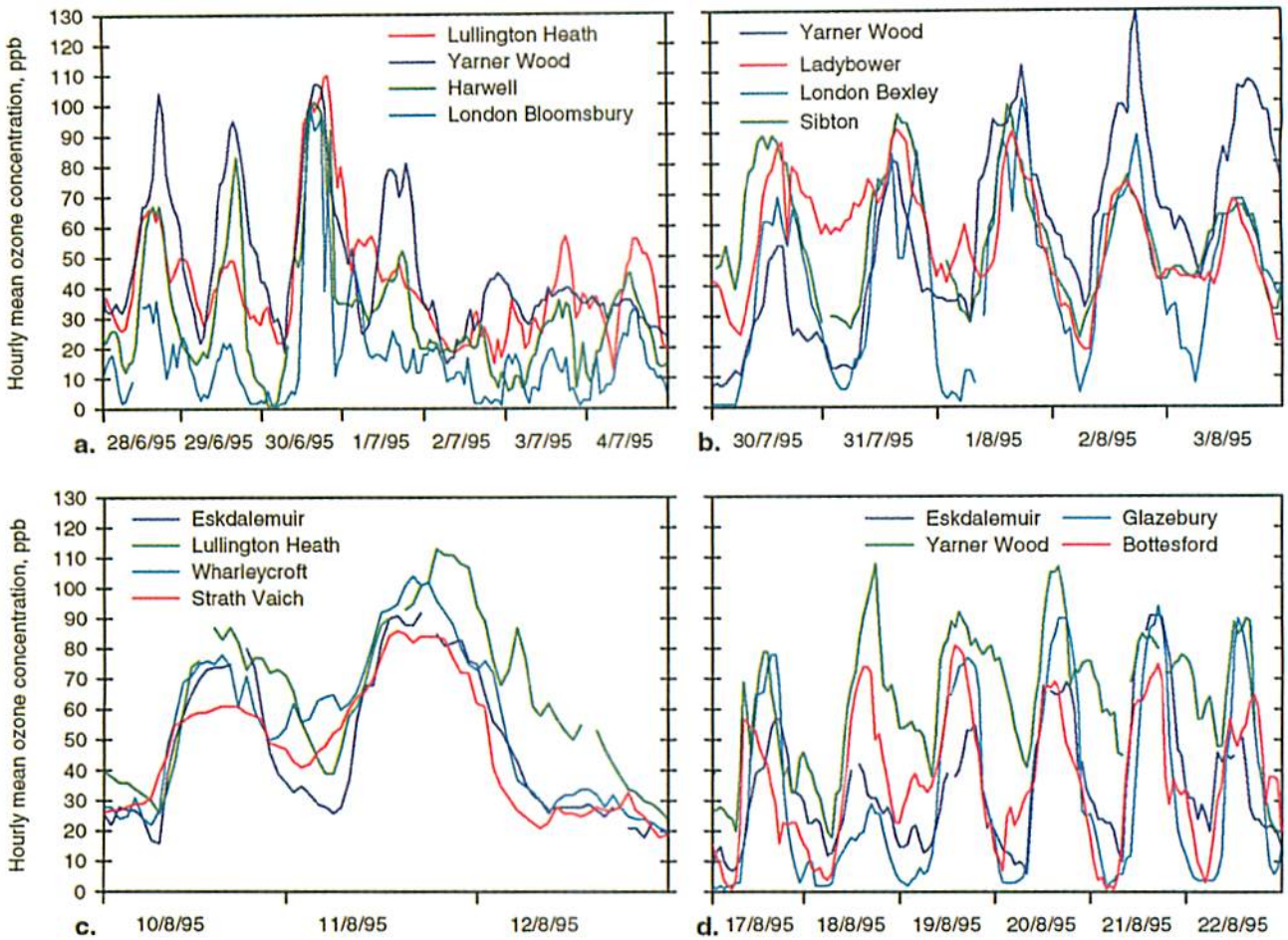


Figure 3.39 Hourly mean ozone concentrations during 4 episodes in 1995.

Air mass back trajectories to the south of England for these episodes show that although the air masses arrived by different routes, on both occasions they had travelled over high emission areas of Europe, where photochemical pollution would have accumulated. On the 27th of June, air masses arriving in south east England appear to have travelled for about 2 days from northern Germany in a looping path, entering the UK in East Anglia, whereas on the 3rd of July the air mass had been in southern Germany before entering the UK in Kent.

The ozone concentrations during 1995 were generally above average for recent years and reached 90 ppb at rural monitoring sites on several occasions during July and August. Some notable episodes occurred:

1. During late June and early July ozone concentrations became elevated at sites in the south of the country, with a peak of 110 ppb at Lullington Heath, 107 ppb at Yarner Wood, 101 ppb at Harwell and 99 ppb at London Bloomsbury, see Figure 3.39a.
2. 30th July to 3rd of August concentrations again rose and exceeded 90 ppb at six rural sites in England, the urban site London Bexley recorded 101 ppb on the 1st of August and Yarner Wood measured the maximum level for 1995 of 130 ppb on the 2nd of August, see Figure 3.39b.
3. 10th - 12th August levels exceeded 90 ppb for a total of 48 hours at nine sites across the country, Eskdalemuir recorded 92 ppb and Lullington Heath, Harwell, Wharleycroft and Bottesford exceeded 100 ppb, see Figure 3.39c.
4. 17th - 22nd of August concentrations again exceeded 90 ppb at seven widely separated sites, Yarner Wood peaked at 106 ppb and Eskdalemuir at 91 ppb, see Figure 3.39d.

Back trajectory analysis for air masses entering the UK during 1995 showed a different pattern to 1976, with the majority of trajectories passing through relatively unpolluted regions, or areas where emissions have been reduced, before entering the UK. On the 1st of August most trajectories had travelled along the Baltic and North Sea coast of continental Europe before entering the country from the east and so, excepting those trajectories to the very south, they are unlikely to have passed over regions with significant emissions. On the 11th of August trajectories more closely resembled those of the 1976 episode but they originated in the Gulf of Finland rather than central Europe. Trajectories arriving on the 21st of August appeared to follow a twisting path from the Atlantic Ocean, around the North Sea and made entry into the UK over East Anglia without passing over areas of continental Europe with large emissions.

Although the meteorological situations were closely similar with regard to temperatures between the summers of 1976 and 1995, this similarity did not extend

to the locations of the anticyclones involved and the broad patterns of air-flows that they would have generated. The summer of 1976 was characterised by slow moving, stagnant air of continental European origin, which entered the UK already polluted with photochemically-generated secondary species. The summer of 1995 was more variable and characterised by more brisk air flows from the north east off the North and Baltic Seas. The air masses entering the UK had a much reduced potential for the photochemical generation of secondary pollutants, as they originated in areas with either low emissions of precursor species or where emissions have been reduced since 1976.

This illustrates the importance of air mass origins on ozone concentrations and trends, as does the previous analysis of the Mace Head data set. On some days ozone concentrations will mainly be influenced by

	June - August 1976 (Met. O, 1976)	June - August 1995 (Met. O, 1995 a, b, c)
Summary of Meteorology	- Anti-cyclone centered on north of N. Sea gave high temperatures across whole country and low wind speeds, generally from central Europe	- Variable anti-cyclonic conditions gave high temperatures across whole country and relatively brisk wind speeds, generally from the NE, ie northern Europe
JUNE	- Initially unexceptional - by 22nd high pressure over S.E England but weather fronts affecting N.W areas - next few days pressure intensified with the anticyclone covering most of the British Isles , by end of month the centre had drifted into the north N. Sea - peak temperature 35.6°C in Southampton - wind direction variable, initially N. Westerly then westerly or southerly, by end of June N. Easterly over South England and Wales - sunshine hours generally above average	- started cool and dull - from 20th high pressure moved north from the Atlantic and by 23rd centered on N. Scotland giving north easterly air flow - high pressure dominated from 23rd to 27th - 28th anti-cyclone moved west into the Mid-Atlantic - peak temperature of 34°C at Worcester and Rickmansworth, mean lower than average in some areas but higher in others - dry with total sunshine hours like temperature high in some areas but low in others
JULY	- high pressure and warm weather persisted until the 8th - 9 - 19th unsettled weather, fronts crossed most areas, 20th large anti-cyclone settled off W. Ireland, giving N. Westerly air flow - from 29th low pressure and cooler unsettled weather - high temperatures first few days peak 35.9° in Cheltenham - winds mostly from south and east until mid-month then occasionally S. Westerly from 19th on mainly from west and north - dry with sunshine hours generally above average	- 1st - 3rd high pressure in mid-Atlantic declined, unsettled weather and north westerly winds - 4 - 6th high pressure built up across S. England then whole of UK, gave warm sunny weather - by 9th high pressure moved to Scandinavia - from 11th - 31st weather unsettled, hot and humid with showers although intermittent cool, dry periods - peak temperature 32.6°C at Heathrow on 31st, mean above average - dry, sunshine hours well above average in some areas such as NE Scotland
AUGUST	- first few days cool, unsettled - by second week UK in belt of high pressure extending from the Azores to Scandinavia, weather hot, dry and sunny - cold front crossed north on 12/13th but high pressure persisted main centre off NE Scotland 14 to 21st - 22nd centre moved over Scandinavia, 25th high pressure moved N.W Scotland, 27th low pressure ended hot spell - winds light and variable, generally W/N. Westerly, N. Easterlies much England/Wales by 3rd week, 22nd light S. Easterly went to N/N. Easterly by 27th - peak temperature over 32°C, mean above average - rainfall below average and sunshine hours well above average in all areas	- initially hot and sunny with high pressure over Scandinavia - high pressure moved to west of Scotland 3rd-7th then drifted eastwards back to Scandinavia by 11th, giving cooler weather in some areas but hot again 8th -10th - 12th cold front crossed country giving patchy rain - anticyclone developed 14th-15th dominated for further week, giving hot sunny weather in most areas - 22nd/23rd cold front moved slowly S.E effectively ending the heat wave - wind initially hot easterly then variable N/N. Easterly - peak temperature 34.3°C, mean well above average (broke records) - very dry with total sunshine hours 60% above average

Table 3.8 Summary of weather conditions during June, July and August of 1976 and 1995.

background levels and emissions of precursors from the UK but on other occasions air masses from Europe may bring in already polluted air greatly increasing the potential for ozone production. Hence the year to year variation in ozone concentrations is greatly influenced by meteorology as well as the emissions of precursor species.

3.6 Ozone Budget for the UK

3.6.1 Estimate of Ozone Dry Deposition Across the UK

The dry deposition of ozone to terrestrial surfaces represents the largest sink for tropospheric ozone. The quantity deposited annually has much more relevance for SO_2, for example than for ozone, since ozone deposition cannot be so easily related to the production in the UK. However, deposition to terrestrial surfaces of such a strong oxidizing agent as ozone may provide a quantitative measure of the chemical weathering of a variety of man-made and natural surfaces including coatings (paint etc.) and epicuticular waxes on vegetation. Also, as ambient ozone concentrations have doubled over the last century, the deposition flux to the surface must also have substantially increased. The new maps of ozone concentration and improved understanding of deposition processes allow the ozone deposition flux to the UK to be calculated as follows.

Equation [x] was derived from the rural network measurements to estimate the annual cycle. Figure 3.40 gives a comparison of the estimated and measured monthly means at all the rural network sites.

This equation was applied to an annual mean map, see Appendix 4, to generate maps of monthly mean ozone concentration at 1 km resolution.

$$O3(m) = O3 + A \sin(\omega m) \quad [x]$$

where:

- O3 = annual mean, the map of the summer mean was used to obtain these values at a 1 km resolution across the UK, see Appendix 4
- A = amplitude of the annual cycle, estimated from the 30 day running means of the rural network measurement data to be 8.5 ppb
- ω = frequency of the cycle = $2\pi/12 = 0.524$
- m = month number (Jan to Dec (-1 to 10))

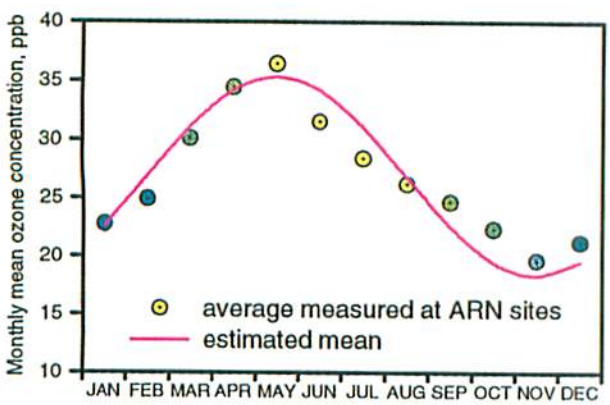


Figure 3.40 Comparison of the estimated annual cycle of ozone concentration with the average of the rural network sites monthly mean for 1988 to 1994.

Equation *xi* was then used to calculate the ozone flux on each 1 km grid square from the monthly mean maps. This flux value was converted into ktonnes of O_3 per month (kt mth^{-1}).

$$F = -O3\ v_d \quad [xi]$$

where:

- F = O_3 flux, $\mu gm^{-2}s^{-1}$
- O3 = ozone concentration in μgm^{-3}, (1 μgm^{-3} = 2.06 ppb (at 1 atm and 10°C))
- v_d = deposition velocity, ms^{-1}, estimated on a 20 km scale using the UK 'big leaf' dry deposition model (Smith *et al*, 1995)

Monthly and hence annual totals were calculated by simply summing the values in each 1km x 1km grid square across the UK. The total amount of ozone deposited was found to be 1484 kt or 30.9 Gmoles and follows a seasonal cycle, with its peak in the summer months, May to July, see Table 3.9 and Figure 3.41. This cycle is mainly due to two processes:

1. The ozone concentration follows an annual cycle with a peak in May and minimum in November, as estimated with equation [x], see Figure 3.40.
2. The ability of vegetation to take up ozone varies with the seasons. During the winter months when the plants' stomata are closed ozone is only deposited to surfaces but in spring plant activity increases and stomata open, allowing greater uptake of ozone molecules by vegetation.

The annual deposition of almost 1500 kt is dominated by the 6-month period March-September when vegetation is actively growing and absorbing ozone along with CO_2. The consequences of absorbed ozone for the yield of crops and other physiological effects in a range of crops and natural species are considered elsewhere in the report. It is however of considerable interest that the deposition of ozone to the UK landscape exceeds, in mass terms, the deposition of any of the other major pollutants (sulphur, nitrogen) by a very large margin. Furthermore if we made the assumption that prior to the 20th century annual mean ozone concentrations were about 10 ppb with a much smaller seasonal cycle, then the ozone deposition to the UK has probably more than doubled over the last 100 years.

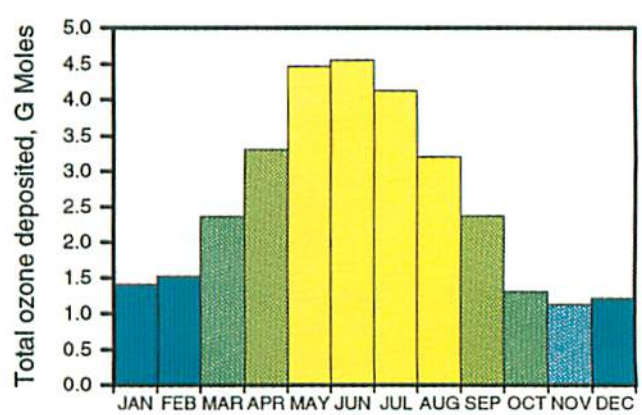


Figure 3.41 Monthly mass of ozone deposited on the UK in Gmoles.

Table 3.9 Mass of ozone deposited on the UK.

Month	ktonnes	Gmoles
JAN	67	1.4
FEB	73	1.5
MAR	113	2.4
APR	159	3.3
MAY	214	4.5
JUN	219	4.6
JUL	198	4.1
AUG	154	3.2
SEP	114	2.4
OCT	62	1.3
NOV	54	1.1
DEC	58	1.2
TOTAL	**1484**	**30.9**

3.6.2 Estimate of Photochemical Ozone Production Across the UK

Simple mass budgets of ozone as air is advected over the UK were presented in PORG 1993 to illustrate some very important features of photochemical oxidant production. In the absence of warm sunny weather the UK is a net sink for ozone over the spatial scale of the country. In this report we have extended the analysis to a larger range of measurement conditions and to more recent data. In this way, taking a very simplistic approach it is possible to use the rural measurement data to illustrate the scale of ozone production and destruction in the boundary layer over the UK for a range of days.

Ozone concentrations at Mace Head were taken to correspond to the background level and so a positive difference between any UK site and Mace Head indicates ozone production and a negative difference indicates destruction. To estimate the mass of ozone generated or destroyed, the analysis is restricted to days

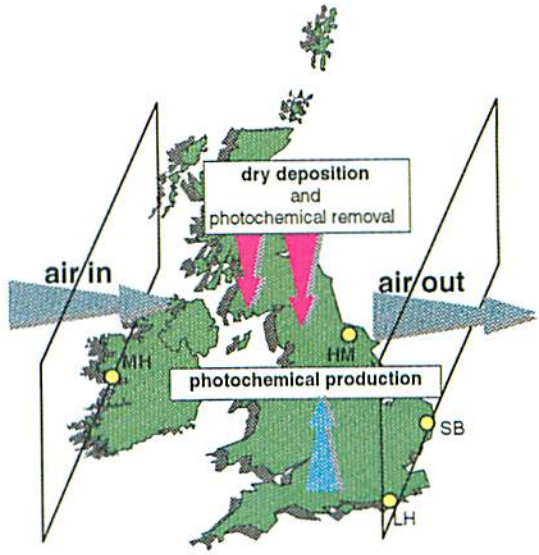


Figure 3.42 Illustration of the influences on the background ozone concentration in an air mass as it crosses the UK.

with westerly air flow, and so the background ozone concentration in air entering the UK is approximately that measured at Mace Head. The difference in concentration between an east coast site and Mace Head therefore gives the quantity of ozone produced or destroyed as the air crossed the UK, see Figure 3.42. To convert this ppb figure into a mass, equation xii is used.

$$O3,\ \mu g s^{-1} = \Delta O3\ k\ l\ h\ u \quad [xii]$$

where:

$\Delta O3$ = difference in ozone concentration at east coast site and Mace Head , ppb

k = 2.06, conversion factor from ppb to $\mu g m^{-3}$ at 1atm and 10°C

l = 600 km, the approximate length of the UK over which most photochemistry occurs (roughly the distance from Edinburgh to London)

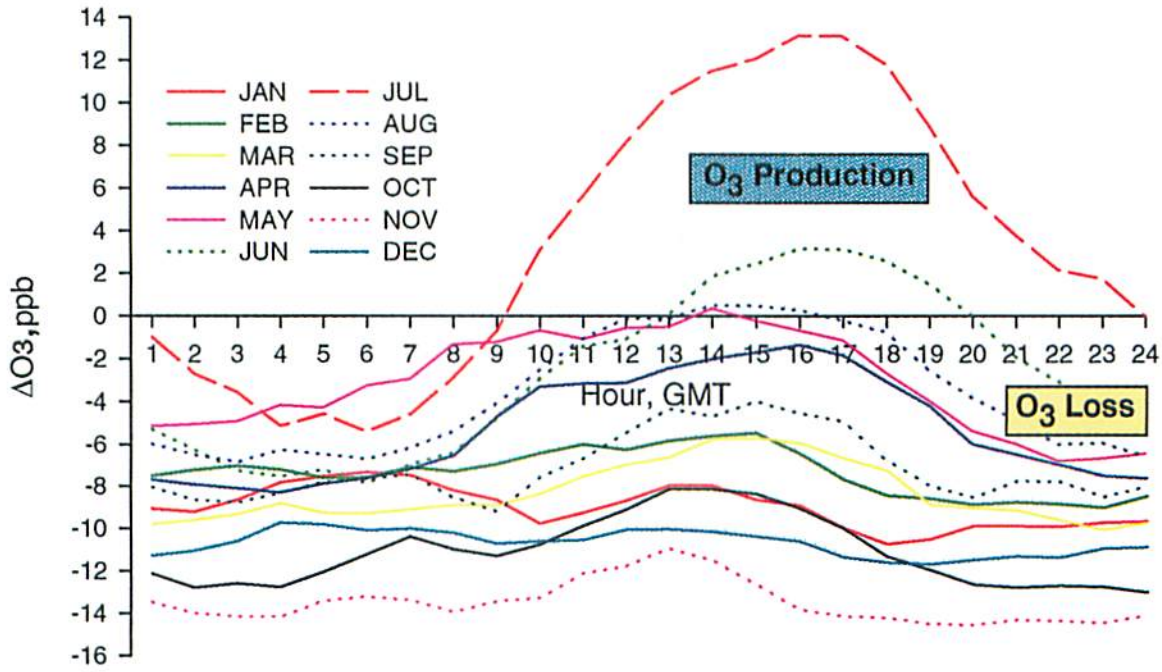


Figure 3.43 Monthly mean of the difference between the hourly average at all sites shown in Figure 3.45 and that at Mace Head.

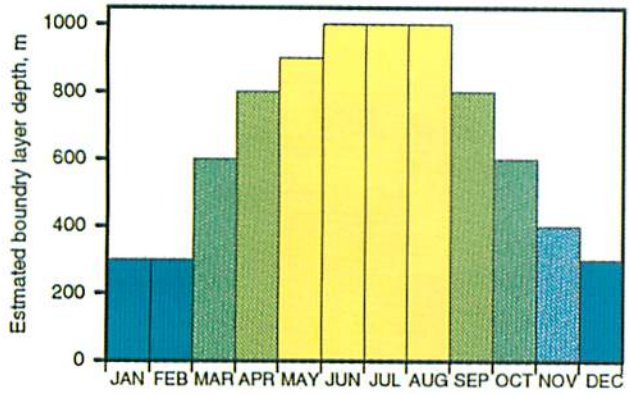


Figure 3.44 Estimated monthly boundary layer depth.

h = estimated monthly average depth of the boundary layer across the UK, see Figure 3.44

u = 10 ms^{-1}, assumed velocity of air traversing the UK

Figure 3.43 shows the diurnal cycle in the average difference between Mace Head and the rural network sites (see Figure 3.45) during 1994, averaged for each month. For most of the year the UK is a sink for ozone as dry deposition and chemical processes outweigh photochemical production. It is only during the summer months of June and July that photochemistry increases and the UK becomes a source of ozone.

High Muffles, Sibton and Lullington Heath were selected as being the sites closest to the east coast, see Figure 3.45. Days with westerly air flow were identified, using the Met Office weather logs and those with data for all 3 sites were selected for analysis. The hourly difference

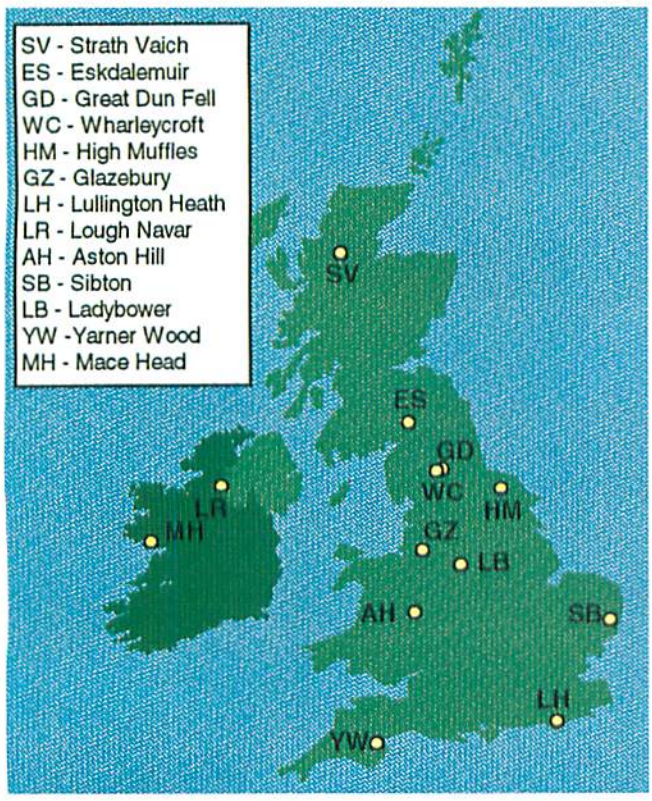


Figure 3.45 Sites used in the analysis for Figure 3.43.

		kt day $^{-1}$			
Julian Day	Date	SB	LH	HM	Mean
2	02/01/94	-2.71	-0.76	-3.93	-2.47
124	04/05/94	-6.37	-2.6	-4.81	-4.59
132	12/05/94	-6.25	-4.45	16.46	1.92
133	13/05/94	-4.89	-5.85	1.8	-2.98
134	14/05/94	-11.53	-20.18	-3.04	-11.58
140	20/05/94	0.12	-3.4	3.68	0.13
158	07/06/94	-15.97	-18.82	-1.2	-12
168	17/06/94	-6.1	-8.85	-11.84	-8.93
169	18/06/94	-3.11	3.29	-4.14	-1.32
170	19/06/94	2.36	7.21	-4.54	1.68
172	21/06/94	-14.55	-3.29	-11.21	-9.68
190	09/07/94	14.82	-7.92	5.56	4.15
193	12/07/94	67.14	53.53	38.4	53.02
195	14/07/94	27.72	17.22	2.45	15.8
205	24/07/94	25.44	30.17	13.66	23.09
206	25/07/94	32.87	2.89	25.41	20.39
207	26/07/94	-4.13	-3.47	-19.8	-9.13
221	09/08/94	-0.62	6.18	-1.51	1.35
222	10/08/94	4.36	2.93	-0.36	2.31
230	18/08/94	-9.17	-2.4	-9.43	-7
231	19/08/94	-6.85	-4.09	-4.14	-5.03
232	20/08/94	-13.62	-7.52	-7.96	-9.7
239	27/08/94	-5.99	-2.76	-8.1	-5.62
240	28/08/94	-9.24	-9.03	-8.41	-8.89
241	29/08/94	-7.89	-9.79	-1.07	-6.25
275	02/10/94	-15.32	-5.93	-8.78	-10.01
278	05/10/94	-16.98	-11.83	-9.16	-12.66
279	06/10/94	-19.76	-5.79	-14.84	-13.46
309	05/11/94	-12.83	-11.53	-14.25	-12.87
313	09/11/94	-8.38	-2.88	-6.5	-5.92
317	13/11/94	-10.13	-3.6	-9.09	-7.61
318	14/11/94	-7.99	-1.45	-3.81	-4.42
319	15/11/94	-8.01	-2.34	-3.92	-4.76
324	20/11/94	-6.71	-3.88	-4	-4.86
341	07/12/94	-5.89	-1.51	-5.26	-4.22
342	08/12/94	-6.17	-2.34	-3.92	-4.14
343	09/12/94	-8.65	-5.35	-8.48	-7.49
344	10/12/94	-5.34	-0.84	-3.59	-3.26
345	11/12/94	-4.3	-2.29	-2.43	-3.01
346	12/12/94	-6.5	-3.64	-2.36	-4.17

Table 3.10 Estimated mass of ozone produced or destroyed in an air mass as it travels from west to east across the UK.

was calculated at each site and equation xii applied, these hourly figures were then averaged and multiplied up to give kt day^{-1}, as shown in Table 3.10. As a fairly high wind speed was assumed no time delay was used to account for the motion of the air mass. This was validated by recalculating some of the values with appropriate time delays and no significant difference was found in the results.

As found from the diurnal cycles in Figure 3.43, production only occurs on days during the summer months, May to August, and for the rest of the year ozone is removed, Figure 3.46. On some days an increase in ozone concentration can be seen as the air moves east, Figure 3.46b, indicating that ozone is being generated faster than the rate of loss. On other days the ozone concentration is reduced as the air moves east, showing that there is little photochemistry

generating ozone. An increase in concentration is particularly clear on July 12th which is the peak day with an average 53 kt of ozone produced, equivalent to 1644 kt mth^{-1}. The mass deposited for July was estimated to be 198 kt mth^{-1} hence photochemical production considerably exceeds deposition for this period. On the 17th of June although a net loss occurred, photochemical production can be inferred as the deficit is reduced as the air moves east, Figure 3.46b.

Taking the days with the maximum excess and deficit ozone concentration for the UK in comparison to Mace Head, 12/7/94 and 6/10/94, a maximum ozone production during the summer of 1644 kt mth^{-1} and ozone loss during the winter of 355 kt mth^{-1} (417 kt mth^{-1} total deficit - 62.3 kt mth^{-1} deposition loss for October) can be calculated.

These very simple mass budgets are purely illustrative, but they make the very important point that the spatial scale of the UK is small relative to the footprint of the atmosphere influenced by UK emissions. The other important feature of the analysis is that for most of the year the UK is a substantial ozone sink. In particular, in cold late spring weather the NO_x and VOC emitted by the UK does not necessarily lead to ozone production over the UK. With more favorable atmospheric conditions further downwind, substantial ozone production may occur from UK emissions over continental Europe and Scandinavia, before the NO_x is oxidized to HNO_3 and can no longer contribute to ozone production.

3.7 Co-occurrence of Ozone and Other Major Pollutants

The assessment of effects of ozone is based almost exclusively on the presence of ozone as a single pollutant. However it is widely recognised that the potentially damaging episodes of ozone occur in combination with other pollutants and systematically with other environmental variables. Photochemical ozone episodes are most commonly associated with enhanced concentrations of PAN, high temperatures, poor visibility and large particulate concentrations.

This section reports some of the relationships between ozone and other pollutants for a site in the PORG network at which continuous measurements are made of O_3, SO_2, NO, NO_2 and the major meteorological variables (Total solar radiation (St), wind speed (U), ambient air temperature (T), wind direction), see Figure 3.47.

The simple regression of NO concentration with O_3 shows the two gases to be negatively correlated, resulting from the rapid NO reaction with O_3 (Figure 3.47b). As other primary pollutants (e.g. SO_2) are positively correlated with NO concentrations at individual sites, there is also a negative correlation between O_3 and SO_2 (Figure 3.47a). For NO_2, which is largely a secondary pollutant, there is also a clear negative correlation with ozone when all data for a year are included in the analysis. The effect of major local NO sources on O_3 concentration at individual monitoring stations is clearly evident in the directional dependence of mean O_3 and NO_2 concentrations. At the Bush Estate monitoring station 10 km SW of Edinburgh, ozone concentrations in NE winds with air from the Edinburgh conurbation are between 5 and 10 ppb smaller than for other wind directions (Figure 3.11 and 3.47e). The 40° sector with mean ozone concentration depressed by 5 to 10 ppb is the sector with ambient NO_2 averaging 6 ppb larger than the other sectors, showing that the NO_2 is largely the Edinburgh NO emissions oxidized by the background 25 ppb ozone concentration. Such analyses however, are crude and fail to identify the relationships between pollutants which may be present for the small fraction of time that ozone concentrations are potentially damaging to vegetation or human health.

3.7.1 Co-occurrence of O_3 and NO_2 when the critical level (40 ppb) is exceeded

A frequency distribution for ozone concentration may be obtained for individual concentration ranges of NO_2 to examine either the likelihood that NO_2 concentration exceeds a given value at a range of ozone concentrations or, the mean NO_2 concentration associated with different ozone concentrations. Such conditional distributions using hourly data for a 6 year period at a single site (Figure 3.48a) show that even though ozone concentration correlates negatively with NO_2 concentration, when peak ozone concentrations occur they tend to occur at NO_2 concentrations that are much larger than the mean at the site. In this case it is clear that the NO_2 concentration during exceedances of the 40 ppb threshold are larger than the mean value by typically a factor of 3.

Table 3.11 Mean co-occurrence concentration of NO_2 with O_3 at Bush during 1988-93.

April - July 1000-1800	
O_3 band, ppb	Mean NO_2, ppb
50 > 60	7.7
60 > 70	10.2
70 > 80	9.4
80 > 90	10.0
90 > 100	18.5
100 > 110	14.3
Mean April - July 1000-1800	
O_3, ppb	NO_2, ppb
35.2	6.3

If the ozone data are separated into a winter period, November-January, when little or no ozone production occurs, then the effects of ozone titration by NO are clear and mean ozone is merely related to NO_2 concentration (Figure 3.48b). By contrast, in spring and early summer daytime conditions the periods of elevated ozone are associated with larger than average NO_2 concentrations (Figure 3.48c). These conditions may be summarized as in Table 3.11 which show that O_3 concentrations in the range 60 to 90 ppb occur in the presence of NO_2 concentrations which are a factor of 2 larger than the mean over the monitoring period. The implications of such co-occurrences for the assessment of effects is briefly considered in Chapter 7 of the report.

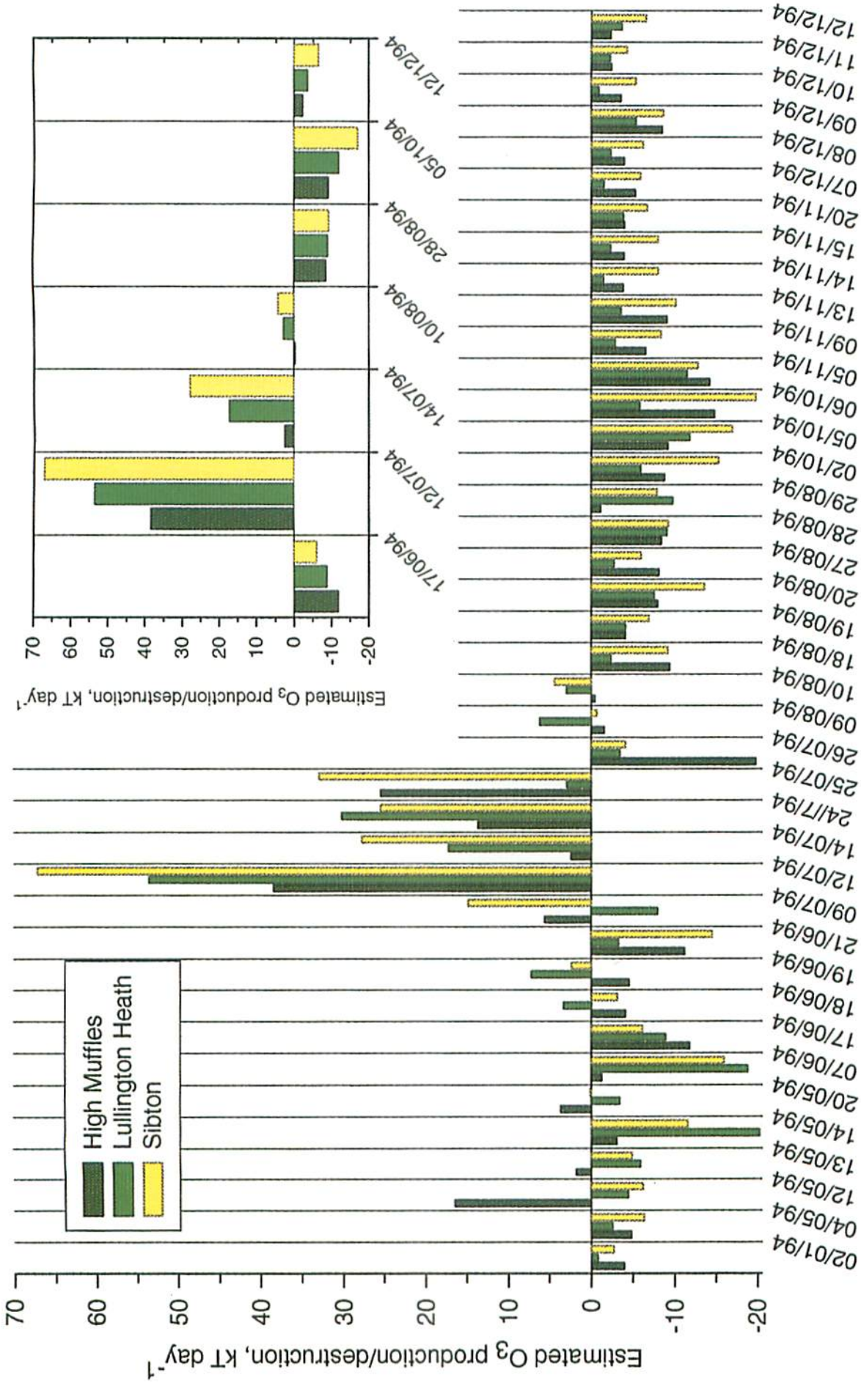


Figure 3.46 Estimated mass of ozone produced or destroyed relative to concentrations at Mace Head on days with westerly air flow.

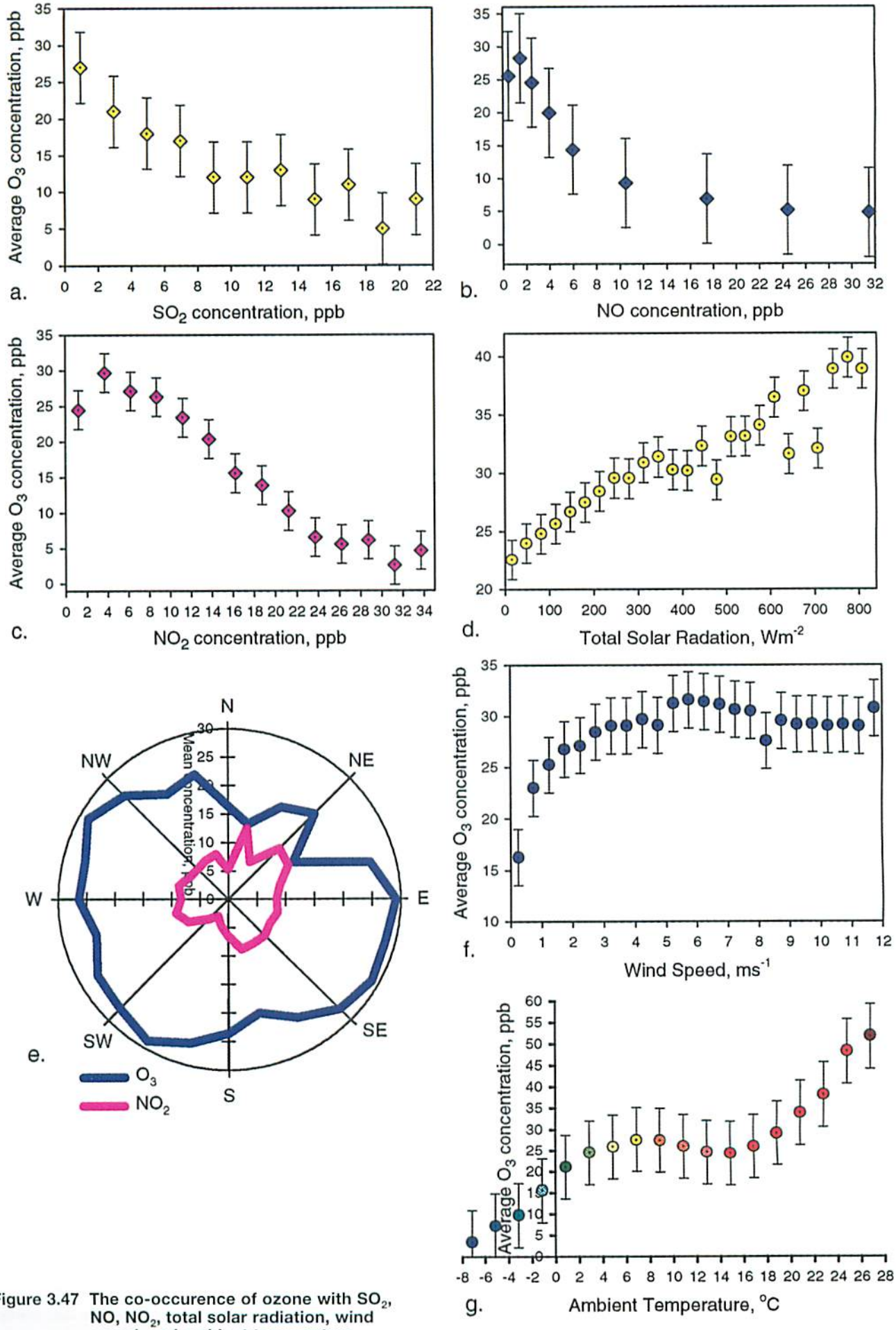


Figure 3.47 The co-occurence of ozone with SO_2, NO, NO_2, total solar radiation, wind speed, and ambient temperature.

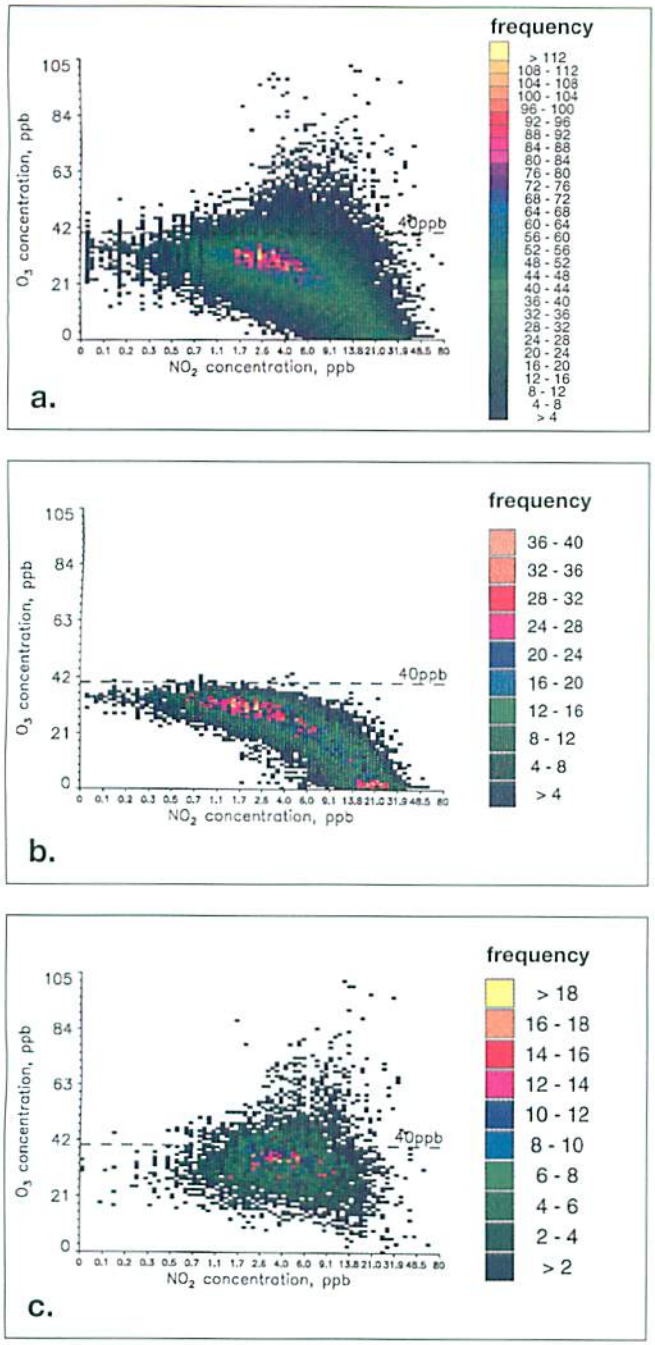


Figure 3.48 Conditional distributions of hourly average O_3 with NO_2 at Bush for 1988 - 93 during the periods: a. all data, b. the winter months November to January, c. the summer months April to July during the hours 1000 and 1800.

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4. OTHER INDICATORS OF PHOTOCHEMICAL POLLUTION

- Peroxyacetyl nitrate (PAN), hydrogen peroxide and nitric acid are the most important products of photochemistry besides ozone, but none is thought to reach damaging concentrations in Britain.
- Hydrogen peroxide concentrations measured at Harwell, Oxfordshire, between 1992 and 1994 show no evidence of a long-term trend since 1988. Average concentrations were 0.2-0.3 ppb, with hourly maximum not exceeding 3 ppb.
- New long-term PAN measurements have been made in eastern Scotland and western Ireland. Annual concentrations (geometric mean) were 50-100 ppt in Scotland and 30 ppt in Ireland, smaller than at Harwell (*ca* 175 ppt). The Harwell data showed no long-term trend between 1987 and 1994, although data capture was poor in 1992-94.
- PAN concentrations were only correlated strongly with ozone concentrations during photochemical episodes. Large (> 0.5 ppb) winter PAN concentrations were not always associated with large ozone concentrations.
- PAN episodes in eastern Scotland occurred when anticyclonic conditions brought polluted air from mainland Europe north over England.

4.1 Introduction

Photochemical reactions produce a wide range of secondary pollutants from primary gaseous emissions. These may be other gases, of which the most important after ozone are hydrogen peroxide (H_2O_2) and peroxyacetylnitrate (PAN). Organic peroxides and higher peroxyacyl nitrates (e.g. PPN, peroxypropionylnitrate) have been measured in ambient air, but are generally present at concentrations close to the detection limit. The available data on hydrogen peroxide and PAN concentration measurements in Britain up to 1991 were presented in the last report (PORG, 1993). A summary of the chemical reactions leading to the formation of peroxides and peroxyacyl nitrates is given in Chapter 2. Other organic nitrates are also formed from reactions of VOCs with NO_x, and contribute to the concentration of total oxidised nitrogen compounds in the atmosphere, known as NO_y. Concentrations of NO_y ($NO + NO_2 + PAN + HNO_2 + HNO_3$ + organic nitrates + particle nitrate +...) can be measured directly (Fahey *et al*, 1985), and give an overall measure of oxidised nitrogen from photochemical reactions. There is often, however, a marked discrepancy between measured NO_y concentrations and the sum of the individual components, where these have been measured independently. The "missing" components of NO_y have not yet been identified, even though the discrepancy has been up to 65% in clean marine tropical air (e.g. Singh *et al*, 1996).

Unlike ozone, hydrogen peroxide and PAN have not been shown to have damaging effects on vegetation at the concentrations experienced in UK. There have been few recent reports of the effects of PAN on vegetation (Cape, 1996), and then only for PAN concentrations of several ppb (e.g. Sun & Huang, 1995). The effects of gas-phase hydrogen peroxide on vegetation have been studied recently at Imperial College, London, and at the University of Lancaster. At Imperial College (Tuckett, 1995), wheat plants were fumigated for 6 weeks with a mean concentration of H_2O_2 of 3-4 ppb, with or without 100 ppb O_3. Although the ozone treatment significantly accelerated leaf senescence, there was no evidence of an adverse effect of H_2O_2, or of any interactive effects of the O_3/H_2O_2 combination. If anything, H_2O_2 increased leaf biomass. At Lancaster University (Terry *et al*, 1995), continuous fumigation of cherry seedlings with 20 ppb H_2O_2 for 8 weeks increased soluble protein levels and the activity of the enzyme glutathione reductase, which is associated with antioxidant systems, in the leaves. These concentrations are, however, very much greater than those observed in the UK.

In addition to gases, particles are produced (sulphate from SO_2 and nitrate from NO_x), which contribute to the haze and reduction in visibility during photochemical episodes, and eventually are incorporated into cloud droplets and become "acid rain". Although concentrations of photochemically-produced gases other than ozone are unlikely to be of importance for either human health or effects on plants, acidic particles have been implicated in causing respiratory complaints (Chapter 7).

4.2 Hydrogen Peroxide Measurements

Data from Harwell for 1988 - 1991 were presented in the previous report (PORG, 1993). Continuous measurements on an hourly basis resumed in May 1992. Daily average concentrations are shown in Figure 4.1 for 1992-1994. As in previous years, maximum daily concentrations were around 2 ppb, with maximum hourly concentrations up to 3 ppb. The maximum values occurred in summer, and overall the distribution of hourly concentrations throughout the year was approximately log-normal. In 1992 (May-December) the average concentration was 0.35 ppb, with geometric mean 0.20 ppb and geometric standard deviation 3.1; in 1993 the average concentration was 0.20 ppb, with geometric mean 0.15 ppb and geometric standard deviation 2.2; in 1994 the average concentration was 0.25 ppb, with geometric mean 0.18 ppb and geometric standard deviation 2.2.

The diurnal variation in concentration of hydrogen peroxide at Harwell was greatest in summer, reflecting the role of photochemistry in producing a mid-afternoon peak concentration. The smaller diurnal variations at other times of the year reflect variations in atmospheric mixing (e.g. depletion during the night below an inversion layer) and photochemical production rates. On a longer time scale there is little evidence for a long-term trend in hydrogen peroxide concentrations (Figure 4.2), as suggested in the last report, when only 4 years data were available.

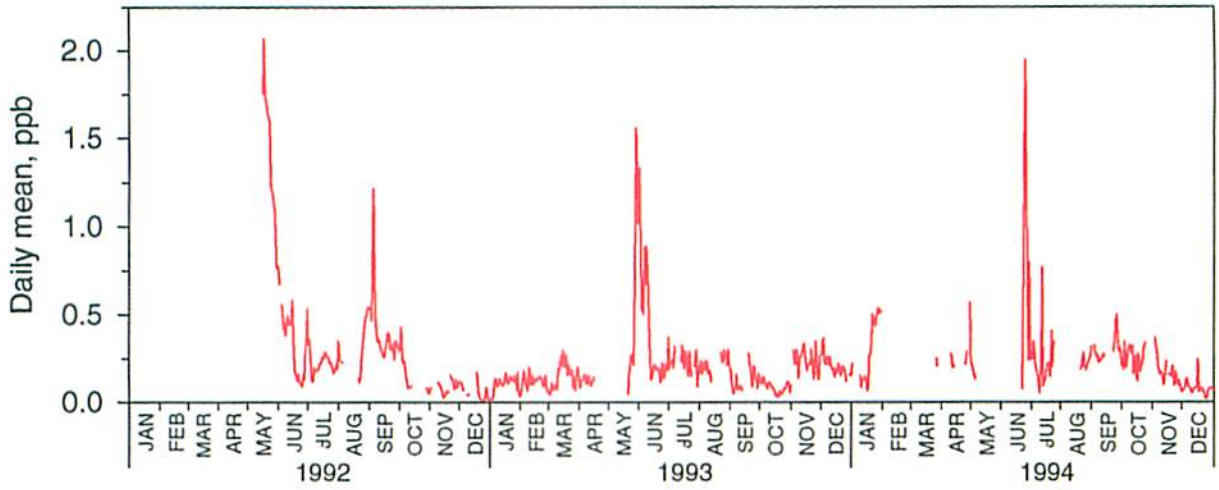

Figure 4.1 Daily mean hydrogen peroxide concentrations at Harwell from 1992 to 1994. Data from AEAT.

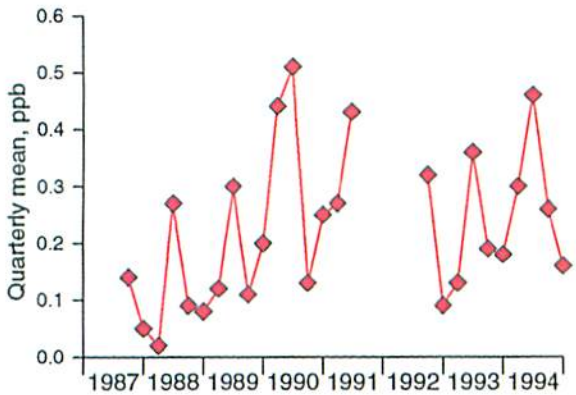

Figure 4.2 Trend in quarterly average hydrogen peroxide concentrations at Harwell from 1987 to 1994. Data from AEATechnology plc.

The continuous measurements at Wharley Croft, Cumbria, described in the previous report are no longer made. There were, however, a few days data from spring 1995 at a nearby site (Great Dun Fell), which showed small average concentrations, up to 0.2 ppb (Table 4.1).

Measurements closer to pollutant sources can be much greater; data from 2 days of sampling at the University of Lancaster showed hourly average concentrations up to 2.5 ppb, with a maximum concentration in the middle of the day (Table 4.1). No organic peroxides were detected. Concentrations measured between May and October in a plantation of young Norway spruce trees at Headley, Hampshire, in 1992 and 1993 showed only small differences between inside and outside the plant canopy, with average peroxide concentrations between 0.4 and 0.7 ppb, and a maximum of 1.6 ppb. However, up to one third of the total measured concentration was attributed to organic peroxides. A similar set of measurements made in and above a wheat field at Ascot, Berkshire, gave average total peroxide concentrations between 0.5 (1992) and 1 ppb (1993), and a maximum of 3 ppb, with around 23% of the total attributed to organic peroxides, Table 4.1, (Tuckett, 1995).

4.3 PAN Measurements

In addition to the continuous measurements of PAN at Harwell, long-term measurements of PAN concentrations

Table 4.1 Hydrogen peroxide measurements in UK 1992-1995.

Location	Date	Time	Average H_2O_2 concentration (range) ppb	Method	Operated by
Headley, Hants	7 days in summer 92	c.1200-1500	0.36*	batch 3 h	Imp. Coll.
Headley, Hants	8 days in summer 93	c.1200-1500	0.68*	batch 3 h	Imp. Coll.
Ascot	11 days in summer 92	middle of day	0.49(0.1-1.4)*	batch 30 min-5h	Imp. Coll.
Ascot	12 days in summer 93	middle of day	0.97(0.3-3)*	batch 30 min-8h	Imp. Coll.
Great Dun Fell	22/3/95	1915-2045	0.21	continuous	UMIST
Great Dun Fell	23-24/3/95	1150-0500	0.12	continuous	UMIST
Great Dun Fell	24/3/95	1130-1800	0.21	continuous	UMIST
Great Dun Fell	30/3/95	0930-1800	0.16	continuous	UMIST
Great Dun Fell	31/3/95	1150-1800	0.08	continuous	UMIST
Great Dun Fell	1/4/95	1040-2200	0.23	continuous	UMIST
Lancaster	12/4/95	1000-1600	1.25 (0.2-2.5)	batch 45 min	Uni. Lanc.
Lancaster	11/5/95	1000-1500	0.9 (0.6-1.5)	batch 45 min	Uni. Lanc.

* total peroxides: at Headley in 1993 organic peroxides were 32% of total (no data for 1992); at Ascot organic peroxides were 25% and 22% of total in 1992 and 1993 respectively.

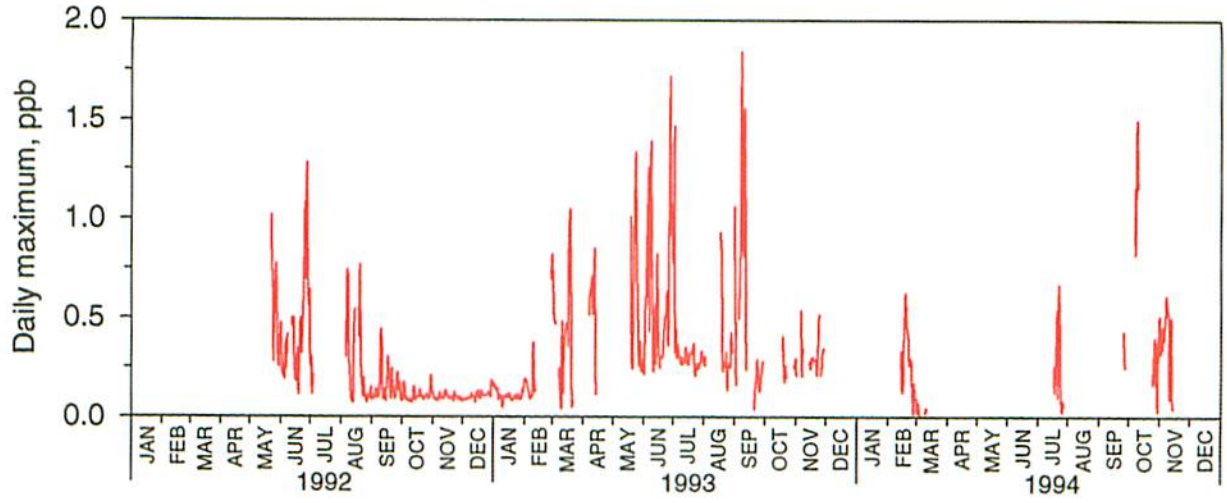

Figure 4.3 Daily maximum PAN concentrations at Harwell between 1992 and 1994. Data from AEAT plc.

have become available from two other sites in the British Isles: Mace Head on the west coast of Ireland, and Bush Estate, 10 km SW of Edinburgh.

4.3.1 PAN in Southern England

Daily maximum PAN concentrations at Harwell were presented in the previous report (PORG,1993) for the period 1987-1991. Figure 4.3 shows more recent data from the same site (1992-1994). Although data coverage was poorer than in the previous period, the picture is rather similar to 1989-91, with daily maximum concentrations not exceeding 2 ppb. There is no clear correlation between periods with large PAN concentrations and periods with large hydrogen peroxide concentrations (Figure 4.1).

There was, however, a correlation with ozone concentrations, as shown in the co-distribution of the two gases in 1993 (Figure 4.4). Simultaneous measurements of both gases were made for only 13% of 1993, and the data in Figure 4.4 are biased towards the summer months, when photochemical production of both gases would be expected to lead to correlated concentrations.

The lack of data coverage precludes the calculation of an accurate annual average concentration, to investigate long-term trends, but the similarity between daily maximum concentrations in 1992-94 and those for 1989-91 suggests that there has been no pronounced trend in concentration over the whole period. This would be consistent with measurements in the Netherlands, where a gradual decrease in annual average PAN concentrations was observed between 1980 and 1994, but with large year-to-year variation, (Roemer, 1996). For 1993, which had 28% data capture of hourly data for PAN, the arithmetic average concentration was 250 ppt.

4.3.2 PAN in Eastern Scotland

PAN has been measured by the Institute of Terrestrial Ecology, Edinburgh Research Station, since 1991. The measurement site at Bush Estate (Appendix 2) is in a rural area, and only rarely exposed to air pollution from the city of Edinburgh to the north-east. Long term average NO_x concentrations are 7 ppb, and

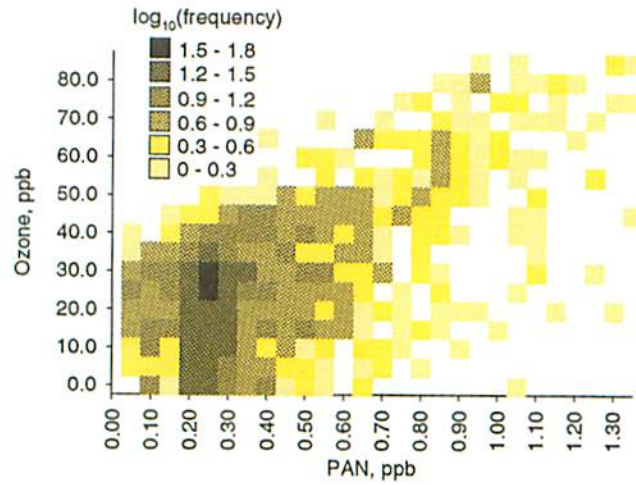

Figure 4.4 The co-distribution of PAN and ozone at Harwell in 1993. Simultaneous measurements of both gases were only available for 13% of the year, mostly in summer. Data from AEATechnology plc.

photochemical ozone events up to around 80 ppb are observed several times each year. Continuous measurements (using gas chromatography with electron capture detection) started in 1994, and although the instrument was occasionally removed for process-based field studies elsewhere, data capture for one-hourly 'spot' sampling was 68% in 1994 and 63% in 1995.

In both years the distribution of PAN concentrations was approximately log-normal, with a geometric mean concentration of 100 ppt in 1994 (geometric standard deviation 2.4) and 50 ppt in 1995 (geometric s.d. 3.6). The arithmetic mean concentration was 150 ppt in 1994 (maximum 1.2 ppb) and 100 ppt in 1995 (maximum 1.9 ppb). This range of concentration is similar to that at Harwell, although the overall mean concentration was smaller. The variation through the year is shown in Figure 4.5, which shows that the distribution of large concentrations was not restricted to the summer months, when photochemical activity would be expected to be greatest. Although rates of photochemical PAN production may be greater in summer, PAN decomposes (to the peroxyacetyl radical and NO_2) more rapidly at

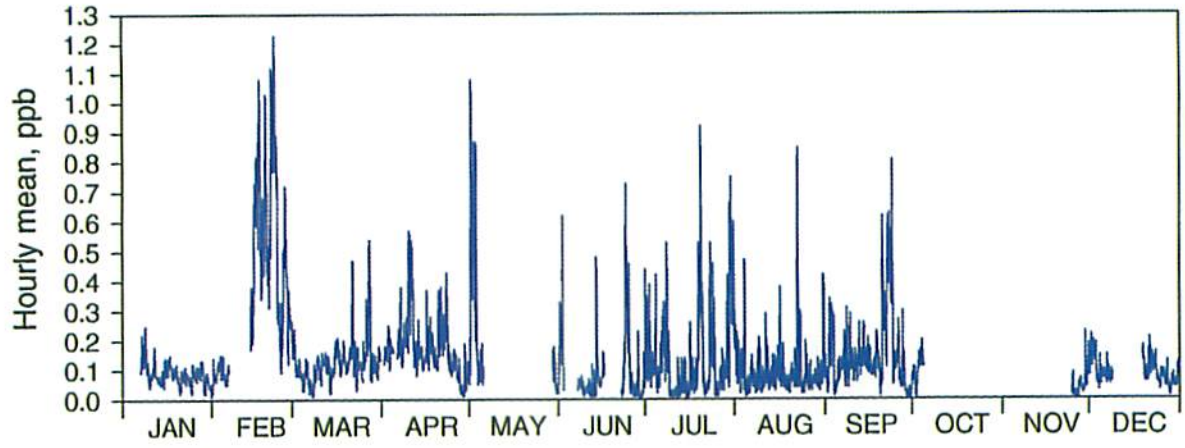

Figure 4.5 PAN concentrations at Bush, eastern Scotland, in 1994. Data from the ITE.

higher temperatures, so that overall concentrations are determined by the balance between production and loss.

The role of photochemistry in forming PAN can be seen from the average diurnal variations in concentration throughout the day (Figure 4.6). For most of the year there is little variation throughout the day in the average PAN concentration, but in late spring/early summer (April to June) there is a pronounced diurnal cycle, with peak concentrations in mid afternoon. The peak in late afternoon is the result of the photochemical processes described in Chapter 2, and the gradual decrease at night shows the effect of thermal decomposition and destruction by deposition at the earth's surface. The diurnal peak in PAN concentration during photochemical episodes, however, does not exactly match the peak in ozone concentration (see Chapter 3, Figure 3.4) , because PAN can be removed from the atmosphere by thermal decomposition, which is rapid relative to loss processes for ozone, such as further reaction or dry deposition. In general, ozone concentrations at Bush were not well correlated with PAN concentrations except during photochemical episodes (Figure 4.7). Large PAN concentrations were sometimes observed even when ozone concentrations were low, although relatively large PAN concentrations were usually observed when ozone concentrations are large. The lack of ozone on some occasions when PAN concentrations were large, usually in easterly winds in winter, may have been caused by localised depletion of ozone by reaction with NO sources close to the monitoring site.

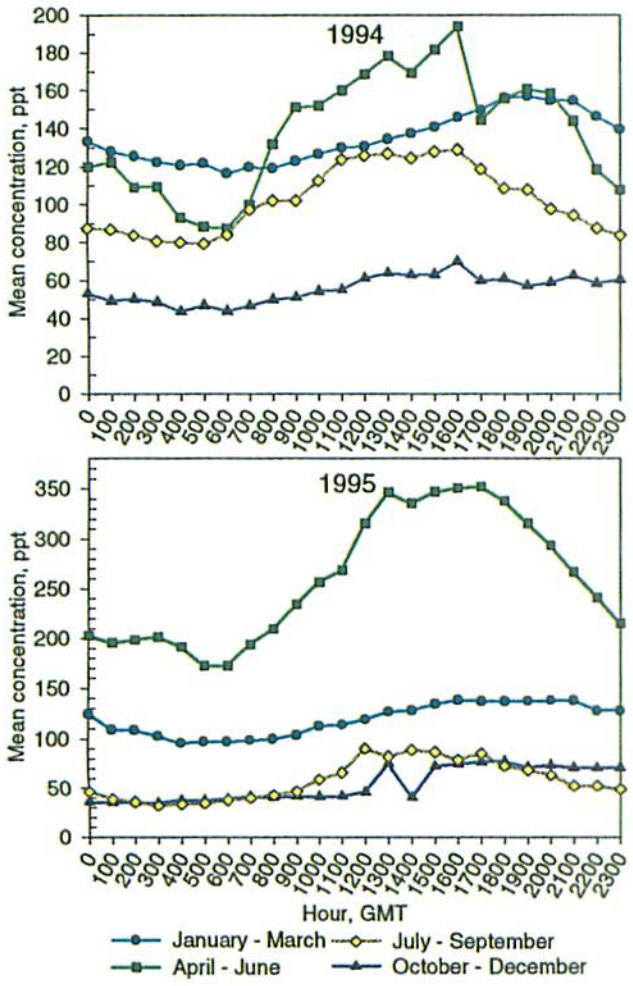

Figure 4.6 Seasonal average diurnal variation in PAN concentrations at Bush, eastern Scotland, in 1994 and 1995. Data from the Institute of Terrestrial Ecology.

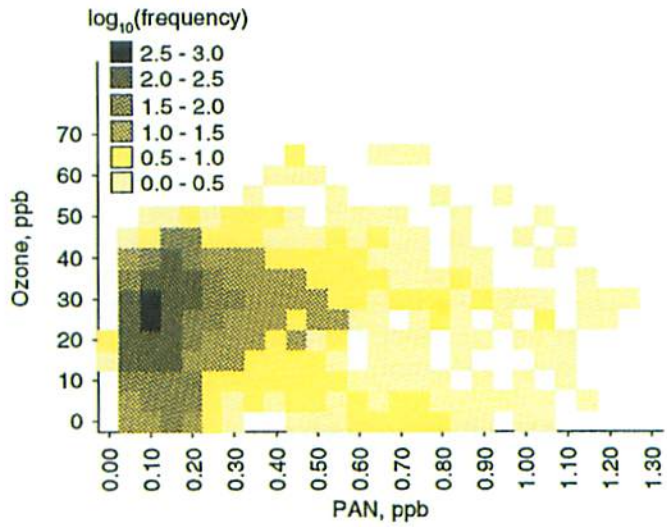

Figure 4.7 The co-distribution of PAN and ozone at Bush, eastern Scotland, in 1994. Data from the Institute of Terrestrial Ecology.

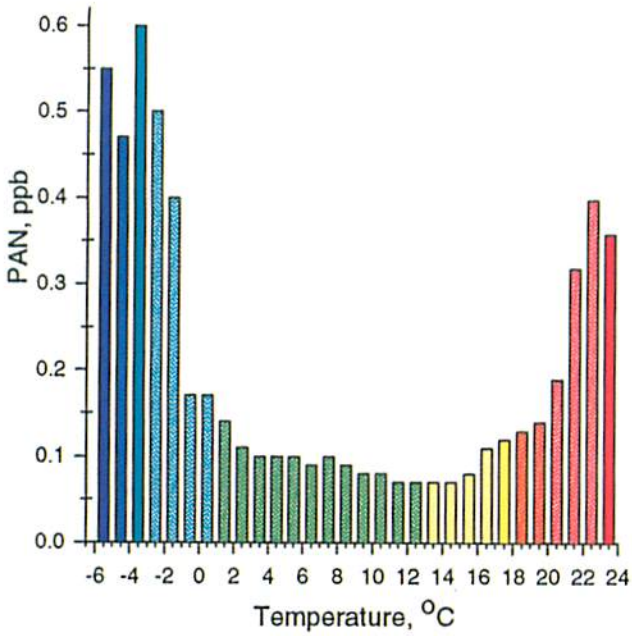

Figure 4.8 The dependence of PAN concentrations on air temperature. Data from Bush, 1994; Institute of Terrestrial Ecology.

The role of temperature in affecting PAN concentrations can be deduced from Figure 4.8, which shows relatively large PAN concentrations when temperatures are low, in winter, allowing the long-range transport of polluted air over long distances without thermal decomposition and loss of PAN from the air mass (see Section 4.3.4). In summer, photochemical activity tends to be greatest on warm sunny days, so that one would expect a positive correlation between PAN concentrations and temperature, when PAN production rates exceed the rate of thermal decomposition. A similar pattern has been observed in data from Paris, (Tsalkani *et al,* 1991).

4.3.3 PAN in Western Ireland

Continuous measurements at 10-minute intervals were started in June 1994 by Simmonds and colleagues, using a gas chromatograph with electron capture detector. The measurement site is at Mace Head, on the west coast of Ireland north of Galway, and co-located with other trace gas measurements of methane, nitrous oxide, carbon monoxide and CFCs. Overall concentrations were similar to those in eastern Scotland, despite the more remote nature of the site. In the second half of 1994 the geometric mean concentration was 30 ppt, and over 1995, for which data capture was better than 75%, the geometric mean was 50 ppt. The distribution was highly skewed to low concentrations, and approximately log-normal, with a geometric standard deviation of 3.2, similar to that for Bush. The distribution is not perfectly log-normal, however, and further investigation of the statistical properties of these data is required. Episodes with high concentrations occurred only in the summer months (April to September), and rarely occurred at the same time as those in eastern Scotland. Figure 4.9 shows a period at the end of April,1995 when there was a very close agreement between PAN concentrations at these two sites, indicative of a homogeneous polluted air mass over the British Isles, but the agreement disappeared in early May, despite both sites continuing to witness enhanced PAN concentrations.

Diurnal variations in PAN concentration were similar to those at Bush, with a marked early afternoon peak in late spring/early summer, and some evidence of a similar peak extending later into the summer. The size of the diurnal cycle varied greatly from month to month, with marked mid-day peaks in April, June and August. There was a better correlation between PAN and ozone at Mace Head (Figure 4.10) than at Bush, probably reflecting the lack of local NO sources which could deplete ozone concentrations while not affecting

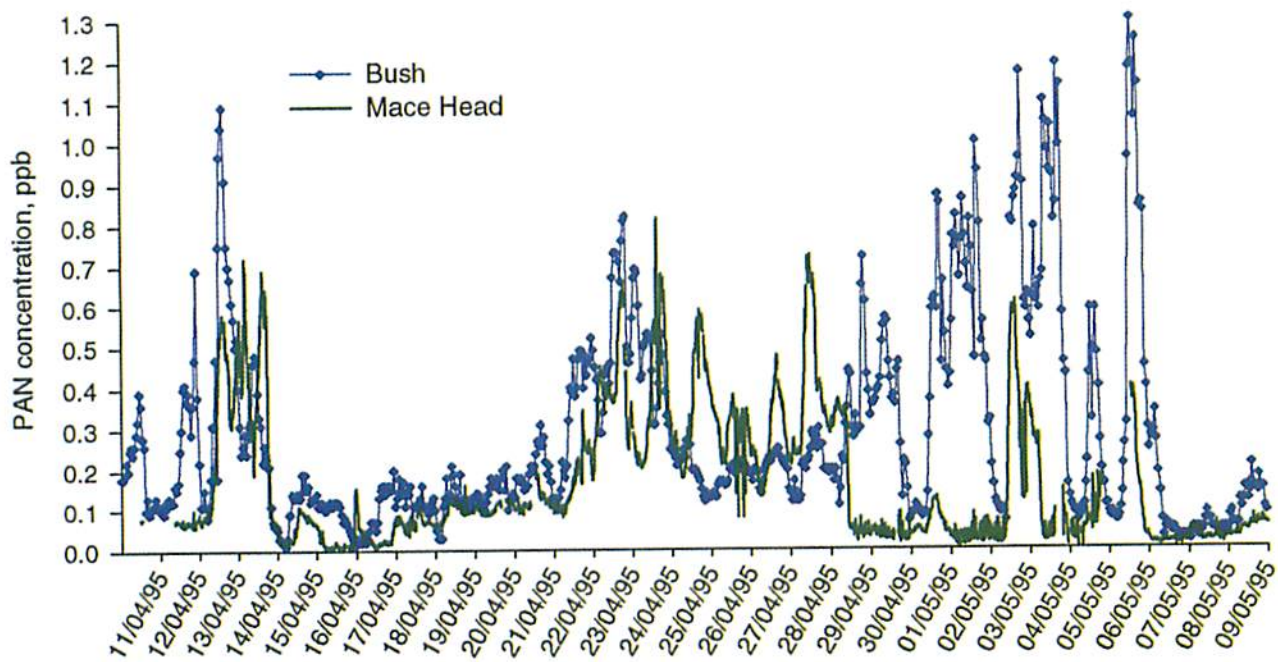

Figure 4.9 Comparison of polluted air (high PAN concentrations) at Mace Head, western Ireland, and at Bush, eastern Scotland, during April and May 1995. Data by courtesy of the Institute of Terrestrial Ecology and Dr. P Simmonds.

PAN. However, the correlation is not strong, with a wide range of possible PAN concentrations for a given ozone concentration, and vice versa.

4.3.4 PAN in Relation to Meteorology

In a study of PAN episodes at Bush Estate, Drummond (1995) analysed the meteorological conditions when PAN concentrations exceeded 0.5 ppb in 1993-1995. On all 6 occasions (Table 4.2) the synoptic meteorology was characterised by high pressure over central Europe, with winds bringing polluted air from continental Europe and England. Back trajectories for these events were constructed and showed a consistent pattern, regardless of time of year. These episodes were marked by a generally polluted air mass. During these episodes the ratio of ozone to PAN, often used as an indicator of photochemical activity, decreased from a typical 'clean-air' ratio of 300-500 to around 50.

However, high PAN concentrations in Britain are not necessarily associated with highly polluted air. During an experimental campaign at Great Dun Fell, Cumbria, in March 1995, enhanced PAN and ozone concentrations were observed in an air mass which contained around 5 ppb NO_x. The episode lasted for 30 hours (Figure 4.11), and the air mass back trajectory indicates that the air originated in the Arctic, before looping round over Britain. The surface (1000 mb) back trajectory crossed Britain from mid-morning on March 22, and reverted to a purely maritime trajectory in the late evening of March 23. Air which passed the site during March 23 had spent up to 2 days over Britain, allowing time for PAN and ozone formation, despite the relatively low temperatures (4-9°C), which may have stabilised PAN, once formed. At the end of this event the ozone: PAN ratio increased from 50 to 500 over a few hours (Figure 4.11).

4.4 Other Indicators of Photochemical Pollution

A wide variety of other atmospheric trace constituents are influenced by photochemical pollution. Acidic particles are formed when SO_2 reacts with the OH radical to give sulphuric acid aerosol (Chapter 2) and when nitric acid (HNO_3) reacts with ammonia (NH_3) to give particulate nitrates. Further information is included in Chapter 6, together with measurements of nitrous and nitric acid gases.

In addition to pollutants derived from the inorganic products of fossil fuel combustion, the atmosphere also contains gases and particles derived from the oxidation of VOCs. Recent measurements of carbonyl compounds (aldehydes and ketones) in Britain are presented in Chapter 5. Further oxidation leads to the production

Table 4.2 Dates of PAN episodes (concentration exceeds 0.5 ppb) at Bush Estate.

A:	28 March 1993
B:	23 February 1994
C:	3 May 1994
D:	21 July 1994
E:	13 April 1994
F:	24 May 1995

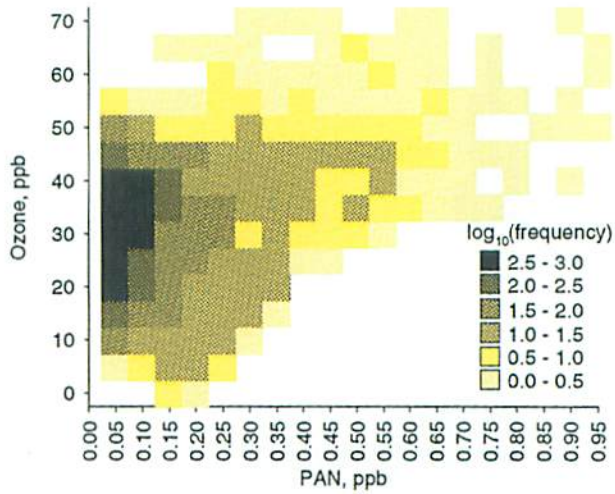

Figure 4.10 The co-distribution of PAN and ozone at Mace Head, western Ireland, in 1995. Data by courtesy of Dr. P Simmonds.

of organic acids, which are not routinely monitored in Britain. Some measurements in air and cloud were made in late spring 1995 at Great Dun Fell, Cumbria, as part of a EUROTRAC-GCE (Ground-based cloud experiment) field campaign; concentrations of formic and acetic acids in air were up to 2 ppb (Laj *et al* 1997). At the same time, concentrations of phenol and nitrophenols in air were measured, up to 10 ppt (Lüttke *et al*, 1997).

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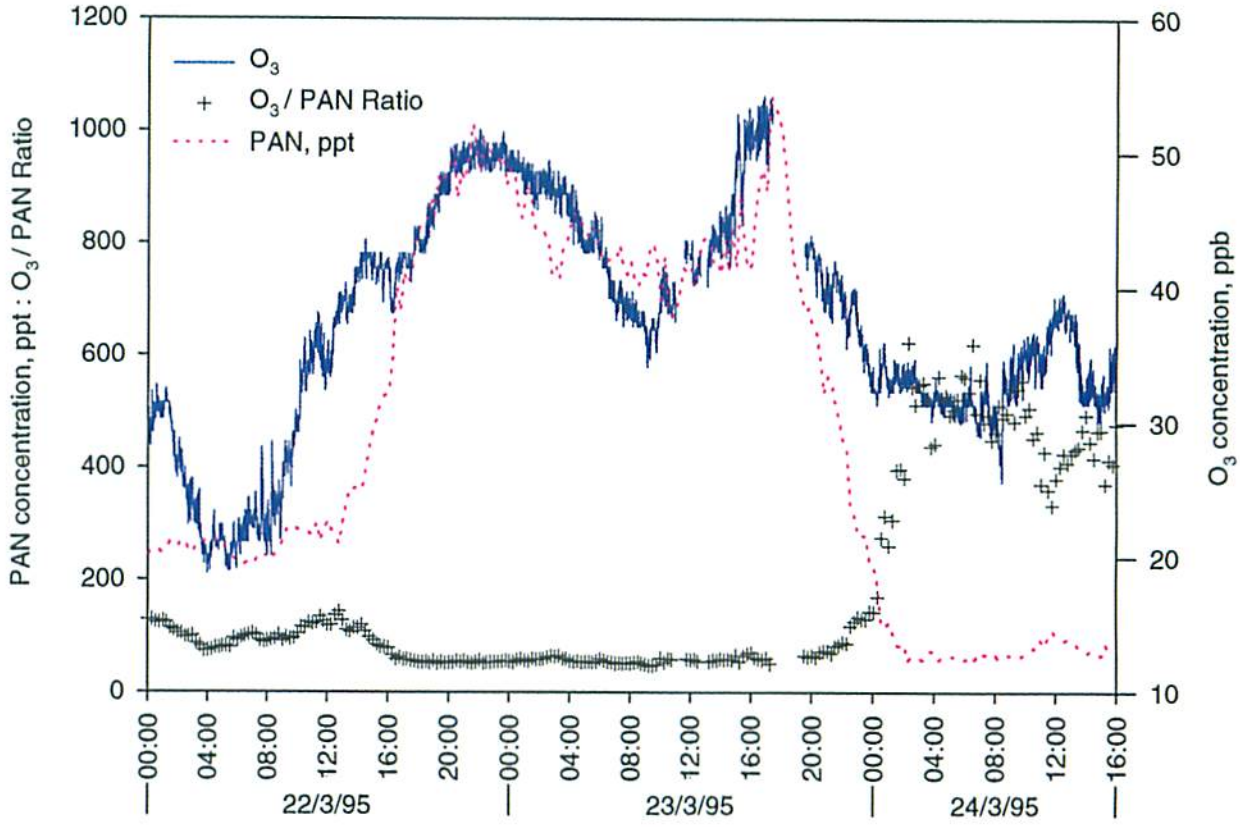

Figure 4.11 PAN and ozone concentrations, and ozone:PAN ratio, during an episode of high PAN concentration in Cumbria, north-west England, during March 1995. Data from Institute of Terrestrial Ecology.

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5. HYDROCARBONS IN THE UNITED KINGDOM

- Total emissions of VOCs in the UK have increased from 2266 kt in 1970 to 2337 kt in 1995. The current inventory indicates that total annual emissions have declined since 1989.
- Mobile sources and solvent usage are the two largest source categories and together account for about 70% of UK emissions of volatile organic compounds.
- Speciated inventories are now available for over 100 VOC compounds.
- Emissions of volatile organic compounds of biogenic origin in the UK were given as 50-100 kt yr^{-1} in the last PORG report. Since then further work has failed to reduce the uncertainty in this estimate, one model predicting less than this and another predicting more.
- The UK has now established a unique national network of hydrocarbon monitoring sites across the UK reporting data hourly on 25 species from 11 urban and 1 rural site.
- Network sites generate data on two carcinogenic compounds, benzene and 1,3 butadiene.
- The UK National Air Quality Strategy has recommended air quality standards for benzene and 1,3 butadiene. Network monitoring data show that current urban concentrations of these compounds are below the standards.
- A complete year of data is available for 1995 and 1996 for most sites and it is apparent that the urban concentrations of the C_2-C_8 hydrocarbons are heavily influenced by motor vehicle emissions and natural gas leakage.
- Local episodes of elevated concentrations are observed at many sites. These are caused by reduced dispersion of local primary emissions of hydrocarbons.
- Measurements of a series of oxygenated hydrocarbons have been made at Harwell, Oxfordshire as part of the EMEP network. Acetone is the most abundant oxygenated hydrocarbon measured and methyl glyoxal the most abundant bifunctional oxygenated organic compound.
- Consideration of rural hydrocarbon measurement data suggest that concentrations may have declined substantially over the period 1970-1990.
- The measured hydrocarbon concentration data have been compared with emission inventories. The automatic measurements point to the national inventory underestimating the emissions of C_2-C_8 hydrocarbons by about 40%.
- Direct, on board measurements of exhaust emissions from motor vehicles are in good agreement with kerbside measurements for all VOCs except acetylene.
- Methane is an important VOC in the atmosphere, making a significant contribution to regional ozone formation. Computer modelling studies have shown that methane accounts for 15-20% of ozone formed photochemically over north West Europe.
- The methane concentrations monitored at Mace Head, Ireland continued to rise up until 1991, when the annual increase slowed somewhat. The increase picked up again in 1994 and 1995; background methane concentrations now stand at about 1805 ppb.
- An analysis has been made of the contributions to photochemical ozone formation which can be sustained by the observed concentrations of 87 individual hydrocarbons reported by the monitoring networks and determined from detailed surveys. The top 10 most important hydrocarbons are i-butene > propene > ethene > isoprene > 1,2,4-trimethylbenzene > m+p-xylene > 1,3,5-trimethylbenzene > *trans*but-2-ene > toluene > *trans*pent-2-ene.
- Biogenic hydrocarbons are unlikely to account significantly for the elevated ozone concentrations observed in the United Kingdom. These will contribute to background ozone concentrations and hence may indirectly influence peak concentrations. Two biogenic hydrocarbons, isoprene and alpha-pinene, have been found to account for 5.5 and 0.4%, respectively, of the ozone forming potential of the observed distribution of hydrocarbons in the United Kingdom.

5.1 Introduction

The role and importance of hydrocarbons emitted by human activities in atmospheric chemistry was established about forty years ago by Haagen-Smit *et al* (1953) in their pioneering studies of Los Angeles smog. The key importance of hydrocarbon oxidation, in the presence of sunlight and nitrogen oxides, as a source of photochemical ozone and other oxidants has been identified through the combination of smog chamber, laboratory chemical kinetics, field experiment, air quality monitoring and computer modelling studies.

Since these early studies, photochemical smog has subsequently been detected in almost all of the world's major urban and industrial centres. However, progress has been slow because sophisticated equipment is required to make valid measurements of the many individual hydrocarbons in the atmosphere and intensive monitoring has only recently become available. There has been a lack of basic information on emissions with which to target research activities.

The situation has improved dramatically over the last few years and the important role played by organic compounds in a range of environmental problems can now be identified. These problems are:

- stratospheric ozone depletion,
- ground level ozone formation,
- toxic or carcinogenic human health effects,
- enhancing the global greenhouse effect,
- accumulation and persistence in the environment.

The nature of the organic compounds involved in these broad environmental issues is very diverse. These compounds are often generically referred to as Volatile Organic Compounds (VOCs). This chapter is primarily concerned with the VOCs involved in the formation of ground level ozone; this subset consists of mostly hydrocarbons. Thus this chapter considers the main sources of hydrocarbons emitted in the UK, their national inventory and recent developments in the monitoring of these compounds. Characteristics of the monitoring data are presented and discussed, with an analysis of current emission inventories for the light hydrocarbons. The roles of carbonyl compounds, methane, higher molecular weight hydrocarbons and biogenic species in the formation of ozone on a regional scale are also considered. Information is presented on the summertime concentrations of hydrocarbons, their likely sources and their potential contribution to ground level ozone formation. It is convenient to divide hydrocarbons into groups due to the large number that have to be considered. The structure of the groups depends on the level of current understanding of their significance and the availability of adequate air quality data to the UK situation.

The consideration of the role played by hydrocarbons in ground level ozone formation, addresses the following groups:

- C_2-C_8 hydrocarbons,
- C_1-C_5 carbonyl compounds,
- methane,
- $\geq C_6$ hydrocarbons,
- biogenic organic compounds.

Use will be made of common names because these are most easily recognised. However, where the IUPAC (International Union of Pure and Applied Chemistry) name differs significantly or where confusion or inaccuracy would result, the IUPAC name is provided in parentheses.

5.2 Sources of Hydrocarbons

5.2.1 The National Atmospheric emissions inventory (NAEI)

The National Atmospheric Emission Inventory estimates atmospheric emissions of pollutants from all sources in the UK. This work is done on behalf of the Department of the Environment, Transport and the Regions by AEA Technology's National Environmental Technology Centre (NETCEN). Pollutants currently estimated include SO_2, NO_x, VOC, HCl, CO_2, particles and heavy metals. Emissions are estimated from 1970 up to the most recent year with available statistical data (currently 1995). Future emissions are also estimated.

Where measured data are not available, emissions have to be estimated. This is true for most VOC emissions. Measurements on a few typical industrial installations enable the emission rate per unit of fuel consumed or product made to be calculated. This rate is called an emission factor. Emission factors used by the NAEI are mainly based on UK or European measurements. For some hydrocarbon sources such as solvent use the emissions can be estimated from the amount of solvent used minus the amount recovered as a liquid waste with an allowance for any control equipment.

There are two main categories of sources of hydrocarbon emissions, road transport and solvent and process emissions. The National Environmental Technology Centre has examined the many solvent and industrial process emission sources of VOCs to provide the best estimates possible. This includes information from industrial trade associations - for example concerning solvent usage, information reported in the open literature, information from surveys of specific industry sectors and information from specially commissioned measurement work. Work on improving these species profiles is continuing and has been reported in full (AEAT, 1995). In the past VOC emissions have usually been reported as a single-valued quantity as if 'VOC' were a single substance. The reasons for this include the prevalence of the flame ionisation detector (FID) as the main means of measurement, a lack of reported data in the literature and the commercial confidentiality of some emissions. The FID is a simple cheap method and frequently nothing more sophisticated is required. Also, many VOC emission estimates were based on mass balances leading to results expressed in tonnes. Now there is a trend towards greater and greater speciation. This is mainly due to the requirements of increasingly sophisticated atmospheric chemistry models and public concerns about the toxicity of individual compounds, such as benzene and 1,3-butadiene. To date nearly 300 compounds have been identified plus 18 sets of other compounds or mixtures including white spirit and kerosene, for example.

Road transport emissions have been measured over the years (e.g. Potter and Savage, 1983; Simmonds, 1989; Farrow *et al* 1993a & b). Emissions depend on the driving behaviour (and hence the type of road and vehicle speed), the vehicle fuel and technology. Emission rates can also be higher when the vehicle starts before the engine warms up. Hydrocarbon emissions are higher from cars without catalysts than from diesel engines. However, with the introduction of three-way catalysts on all new petrol engined cars the emissions from hot engines are comparable; when cold the catalysts do not work efficiently and so the emissions from cold petrol engines are higher than from diesel engines. Data from these measurement programmes have been used to produce an emissions model that takes into account the changing composition of the vehicle fleet and the traffic flows on different types of road. A more limited measurement programme (e.g. Bailey and Schmidl, 1989) has enabled estimates of individual hydrocarbon species to be made.

A summary of the UK emissions of VOCs from 1970 to 1995 is given in Table 5.1 for UNECE source categories. In order to illustrate any trends in the data they are plotted in 6 main categories in Figure 5.1. It is evident that the overall emissions have increased since 1970, peaking in 1989. This trend has been driven by the growth in the road transport sector.

Since 1989 emissions have declined in the road transport sector resulting in an overall reduction in emissions. It should be noted that the solvent use and process emissions data are very uncertain as work is focused on current emissions and changes likely to

Table 5.1 UK Emissions of VOC (kt C yr^{-1}) by UNECE Category

Year	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95
1. Public power etc.	2	2	3	3	3	3	3	3	3	3	3	2	2	2	2	2	2	3	3	3	3	3	3	4	4	5
Coal	2	2	2	2	2	2	2	2	2	2	2	2	2	2	1	2	2	2	2	2	2	2	2	2	2	2
Fuel Oil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Other	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	2	3	3
2. Comm/Inst/Road Combustion Plants	232	201	167	166	159	132	126	130	119	122	102	97	96	90	73	94	99	84	68	60	52	54	50	49	39	32
Domestic	228	197	164	163	156	130	124	128	116	119	100	95	93	87	70	91	97	82	65	58	50	52	48	47	37	30
Other	4	3	3	3	3	2	2	3	3	3	3	2	3	3	3	3	3	3	3	2	2	2	2	2	2	2
3. Ind Comb Plants/Process with Combustion	36	32	28	29	27	25	26	24	23	24	18	18	17	17	15	18	18	18	19	18	17	17	16	16	16	15
Refineries	1	1	1	1	2	1	1	1	1	2	2	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2
Iron and Steel	10	9	8	9	7	7	7	6	6	7	3	4	4	4	4	5	4	5	5	5	5	4	4	4	4	4
Other	25	22	19	19	18	17	17	16	15	15	13	12	12	11	10	12	12	11	12	11	11	11	10	10	9	9
4. Non-Combustion Processes	352	354	356	362	360	350	353	351	354	357	349	343	340	339	339	337	337	337	341	345	346	349	349	345	345	345
5. Extr/Distr of Fossil Fuels	95	102	112	120	119	118	134	167	196	224	229	239	257	273	291	296	302	308	309	286	287	287	292	306	331	334
Petrol Marketing	78	82	87	93	91	89	93	95	101	103	105	103	106	108	111	112	118	122	128	129	126	124	124	119	114	110
6. Solvent Use	700	699	709	748	744	701	719	726	728	724	681	654	653	665	676	684	688	716	767	780	761	729	699	704	705	700
7. Road Transport	563	595	626	658	641	644	676	688	717	719	759	770	789	784	812	820	854	900	951	1000	978	967	912	836	761	690
Petrol Exhaust	382	407	403	453	440	446	468	480	499	498	535	552	571	563	583	588	614	645	685	735	722	720	682	627	575	523
Petrol Evap.	81	85	90	96	94	92	96	99	105	107	110	108	111	113	117	118	124	128	135	139	141	139	135	123	108	95
DERV	101	104	106	109	107	106	111	109	113	114	114	110	107	109	113	113	116	127	131	130	115	108	95	86	79	72
8. Other Transport	151	150	156	165	146	143	143	142	143	145	137	130	133	131	129	131	129	127	129	128	125	128	129	126	126	121
Off Road Sources	119	120	127	134	115	114	114	114	115	117	110	106	106	105	102	105	103	103	103	101	99	101	102	100	100	96
Military	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	1	1	1	1
Railways	13	13	12	13	12	11	11	11	11	11	10	10	9	10	9	9	9	9	9	8	8	8	8	8	8	8
Shipping	16	15	14	16	15	14	14	13	13	14	13	10	13	12	14	13	12	11	11	13	13	13	14	13	13	12
Civil Aircraft	1	1	2	2	2	2	2	2	2	2	2	2	2	3	3	3	3	3	3	3	4	3	4	4	4	4
9. Waste Treatment & Disposal	54	54	54	55	55	55	55	56	56	56	57	57	57	57	57	57	57	57	57	57	52	48	42	27	27	26
10. Agriculture	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11. Nature	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
TOTAL (x 10)	227	227	229	238	233	225	231	237	242	245	241	240	242	244	247	252	257	263	272	276	270	266	257	249	243	234

occur in the near future rather than historic trends since 1970. While increasing use and rising industrial output would be expected to increase these emissions, more efficient use and improved working practices will have reduced emissions. The overall effect of these two opposite processes is unclear. In any event the uncertainties in the emissions from this sector are large, possibly of the order of ±50% and thus swamp any likely trend since 1970. The solvent emissions shown in Figure 5.1 are constant over this period; in practice they are likely to have increased over the period, but remain to be quantified.

An important aspect of gaining information on speciated emissions of VOCs is that this provides the required data for increasingly sophisticated models of tropospheric chemistry. These are capable of calculating the contributions of individual VOC species (based upon emissions and reactivity) to the formation of photochemical ozone. Table 5.2 lists the latest NAEI speciated data for 50 VOCs, that have been used to determine photochemical ozone creation potentials (POCPs, see Chapter 2).

Currently emissions are reported either as national totals or spatially disaggregated over a 10 x 10 km (Ordnance Survey) grid. The spatial disaggregation currently estimates emissions as point or area sources. The spatial distribution for the area sources is estimated by disaggregating the total UK emission estimates by suitable normalised surrogate statistics, such as estimates for road transport (derived from county vehicle kilometres and then split into 10 x 10 km grid squares by population). Other data include population, land-use, smoke-controlled areas, small industry, railways, and coastal shipping. Point source data are added where available for sources such as municipal solid waste incinerators, electrical supply industry and refineries.

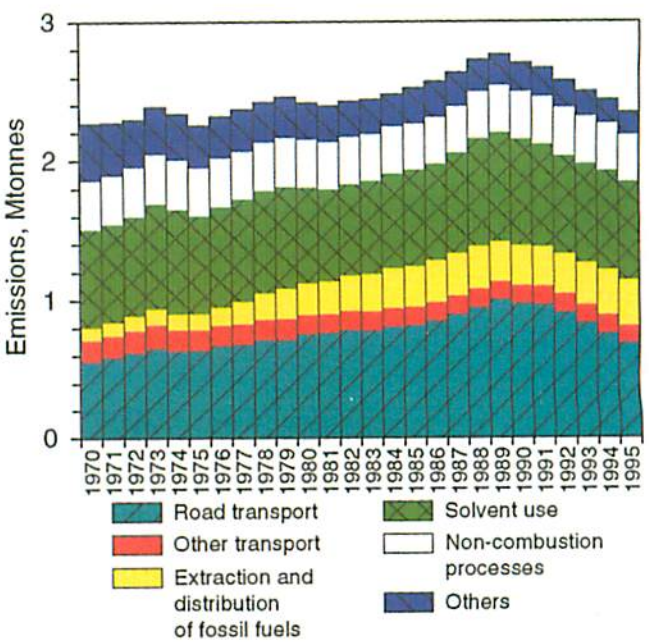

Figure 5.1 Emissions of VOC by UNECE source category.

Figure 5.2 summarises UK VOC emissions on a 1 x 1 km grid scale. The distribution of emissions follows the location of industrial and population centres. There is an intense band of emission stretching from London and the South East through the Midlands to the North West. The use of GIS systems for spatial mapping allows detailed spatial statistics to be used and the inclusion of irregular area sources, such as population statistics

Table 5.2 1995 National Atmospheric Emissions Inventory (NAEI) NMVOC* Speciation kt C yr^{-1}

Emissions of the 50 most significant NMVOCs	Road Transport DERV	Road Transport Petrol	Petrol Evaporation	Other Transport (5)	Off Road (4)	Stationary Combustion	Extraction and Distribution of Fossil Fuel	Processes	Solvent Use	Waste Treatment & Disposal	TOTAL
1,1,1-trichloroethane									19.3	0.25	19.64
1,2,4-trimethylbenzene	0.36	13.7	1.51	0.09	0.83		0.08		7.10		23.75
1-propanol									15.6	0.15	15.85
2,2-dimethylpropane							11.7				11.79
2-butanone									13.8	0.05	13.93
2-butene		8.84	2.41		0.50		0.66				12.41
2-methylhexane		6.65	0.87		0.38		0.48		0.34		8.72
2-methylpentane	1.51	9.94	2.86	0.39	0.79		2.51		0.43		18.43
2-pentene		4.40	2.22		0.25		0.95				7.82
2-propanol									23.6	0.06	23.67
3-methylhexane		5.29	0.88		0.30		0.89		0.69		8.05
3-methylpentane	0.79	6.91	1.90	0.20	0.51		2.58		0.39		13.28
4-methyl-2-pentanone									8.31		8.31
acetone	1.44	0.42		0.72	0.25	0.44			6.93	0.00	10.21
acetylene	2.30	24.6		0.59	2.87	0.51		0.15			31.07
aliphatic hydrocarbons unspecified									17.9		17.93
aromatic hydrocarbons unspecified									10.7		10.76
benzene	0.44	22.8	2.02	0.20	2.50	2.40	1.29	2.89	0.26	0.16	35.00
butane	2.87	18.4	18.9	0.97	1.48	4.45	90.9	21.0	24.9	0.13	184.30
butanols									7.22		7.22
butyl acetate									10.8	0.08	10.97
dichloromethane									32.4	0.27	32.69
ethane	0.36	4.87		0.09	0.89	4.80	18.3	3.46			32.82
ethanol								55.8	41.7	1.14	98.80
ethyl acetate									16.3	0.09	16.46
ethylbenzene	0.57	20.4	1.25	0.15	1.24	0.45	0.14			0.49	24.75
ethylene	7.90	40.9		2.81	3.61	2.02		0.42			57.69
formaldehyde	4.24	4.50		2.56	0.99	6.77					19.06
glycols unspecified									11.9		11.96
heptane		3.56	0.66	0.00	0.20	0.70	23.5	1.93	0.61	1.49	32.70
hexane	0.72	8.22	1.91	0.32	0.57	1.56	20.7	4.74	14.1	0.89	53.84
isobutane	1.44	8.43	9.92	0.37	0.69	1.03	13.6	8.97			44.52
isopentane	3.02	25.1	9.60	0.77	1.88	2.74	12.1				55.31
m-ethyltoluene	0.36	6.02	0.61	0.09	0.39		0.05				7.52
m-xylene	0.57	31.2	1.78	0.15	1.85	0.95	0.25		6.25		43.05
methylheptanes		25.9	0.63		1.47		0.04				28.04
o-xylene	0.57	24.5	1.50	0.15	1.48	0.29	0.20		6.25		34.99
octane		3.24	0.26		0.18		20.4		0.04		24.19
p-ethyltoluene	0.36	6.02	0.61	0.09	0.39						7.47
p-xylene	0.57	31.2	1.78	0.15	1.85		0.25		6.25		42.10
paraffins other					40.5						40.57
pentane	2.01	8.58	6.83	0.56	0.79	5.67	47.0	9.75	15.9		97.23
pentane (isomers)				0.05		1.22		10.8			12.07
propane		1.10		0.01	0.63	2.82	37.3	16.4	24.9	0.00	83.33
propylene	2.44	20.3		0.63	1.52						24.94
tetrachloroethene									10.8	0.49	11.32
toluene	0.57	70.6	5.36	0.15	5.77	1.72	1.57	1.35	60.0	0.66	147.86
trichloroethene									17.6	0.24	17.92
white spirit									98.6		98.62
xylenes(1)						0.21			24.7	0.72	25.67
Total	**35**	**467**	**76**	**12**	**78**	**41**	**308**	**138**	**558**	**7**	**1721**
Other NMVOC Species (2)	**7**	**47**	**7**	**4**	**15**	**9**	**23**	**19**	**116**	**10**	**257**
Total Speciated	**42**	**515**	**83**	**16**	**92**	**50**	**332**	**157**	**673**	**18**	**1978**
Unknown NMVOC (3)	**30**	**9**	**11**	**8**	**5**	**2**	**2**	**177**	**26**	**9**	**279**
TOTAL	**72**	**523**	**95**	**24**	**97**	**52**	**334**	**335**	**700**	**26**	**2257**

Emissions in kt 0.0 ~ < 0.05 kt
Does not include forest emissions (80 kt)

* NMVOC ≡ VOC compounds excluding methane

(1) Unspeciated Mixtures of m,o and p Xylene

(2) Total of Remaining Speciated NMVOCs

(3) May contain contribution from species listed and/or "Other NMVOC Species"

(4) Off road includes naval shipping and military aircraft

(5) Other Transport includes shipping railways and civil aircraft

at Enumeration District level and line sources such as roads and railways. The spatial estimates have more detail and flexible outputs. In addition this allows the incorporation of data collected on individual plant from public registers and other sources. Spatial analysis and validation will also be possible.

5.2.2 Biogenic Organic Compounds

In the 3rd PORG Report, it was recognised that volatile organic compounds, which may contribute to ozone formation and other photochemical processes, occur in the atmosphere as a result of emissions from human activities and vegetation. A biogenic VOC emission rate of 50-100 kt y^{-1} was estimated for the UK, with emissions of monoterpenes probably exceeding those of isoprene. Since 1993, further measurements of emission rates and two major modelling studies have been carried out, giving estimates of biogenic VOC fluxes for the UK.

In the UK, the most abundant tree species is Sitka spruce, being the principal species over an area of about 530 k ha or 25% of the total woodland area (excluding isolated trees, clumps and linear features) in the country (Hewitt and Street, 1992). Its prevalence makes the acquisition of good estimates of monoterpene and isoprene emission data important if uncertainties in emission estimates for the country are to be minimised, and this has now been achieved (Boissard C. and Hewitt C.N. pers. comm.). Emission measurements were made from Sitka spruce in plantations in NW England and SW Scotland utilising three different measurement techniques and reasonable agreement was seen between the results obtained by the three methods. The first of these, the bag enclosure method, gives emission data at the branch scale, but the homogeneous nature of the vegetation in plantations allows extrapolation to the canopy scale. The other two techniques, the micrometeorological gradient method and the relaxed eddy accumulation, or conditional sampling, method, give data on the canopy scale. Additional data were obtained in greenhouse experiments.

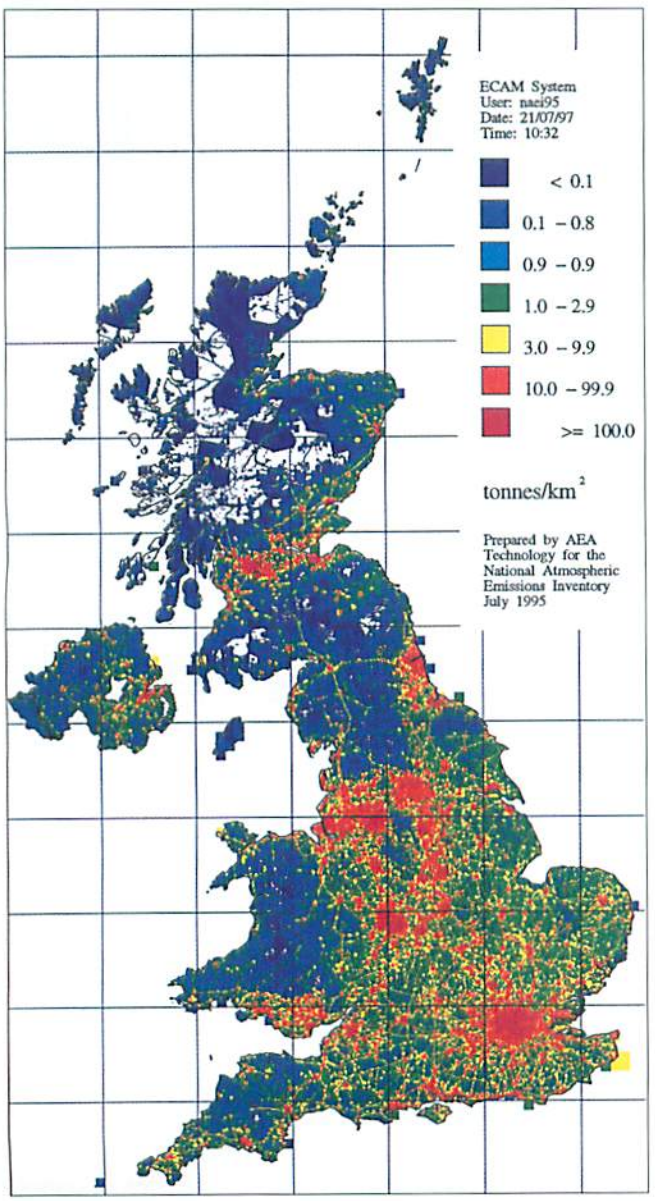

Figure 5.2 1 km x 1 km spatially disaggregated VOC emissions for 1995.

When the measured emissions of isoprene from Sitka spruce were normalised to an ambient temperature of 30°C and a photosynthetically active radiation (PAR) level of 1000 μ mol m^{-2} s^{-1} (necessary for comparisons and modelling because of the strong dependence of VOC emission rates on these parameters) rates of 2 - 7.5 μg g(dry weight)$^{-1}$ h^{-1} were obtained. In addition, at least this amount of monoterpenes (mainly α- and β-pinene, β-myrcene and another compound, either β-thujene or β-phellandrene), was also emitted.

These data, with others from the literature, were used with VOC emission algorithms and meteorological data from the EMEP MSC-W (see Chapter 8) ozone model to generate emission estimates of VOCs for European ecosystems over several summer periods (Simpson *et al*, 1995). Overall, European emissions were estimated to be ~4000 kt C y^{-1} for isoprene and ~6000 kt C y^{-1} for other VOCs, the estimate for isoprene being approximately 50 - 100% greater than previous estimates. Emissions from the UK for the modelled year of 1989 were estimated to be 23 kt C y^{-1} for isoprene (19 kt C y^{-1} in 1990) and 29 kt C y^{-1} for other VOCs.

Guenther *et al* (1995) produced a global model to estimate biogenic VOC fluxes with a 0.5 x 0.5 spatial, and hourly temporal, resolution, using global gridded data sets of ecosystem type, vegetation indices, precipitation, temperature and cloudiness. Flux estimates for the UK for the year 1990 were 110 kt C y^{-1} isoprene, 145 kt C y^{-1} monoterpenes and a total of 320 kt C y^{-1} for all reactive biogenic VOCs.

Uncertainties in these model estimates remain considerable, being at least a factor of three for annual estimates and more (perhaps 5 - 10) for short-term estimates used for ozone episode modelling. The difference between the two model estimates arises mainly from differences in the land cover estimates and meteorological data used. On the global scale, the sensitivity of photochemical models to biogenic VOC emission rate (which are far in excess of other VOC emission rates) indicates a need for a further reduction in the uncertainties in these estimates. On the regional scale, in areas where emissions of biogenic VOCs are

small compared with those from human activities (such as the UK), long-term (seasonal) modelling of ozone formation may not be particularly sensitive to biogenic VOC flux estimates, but short-term, episodic, modelling will remain very sensitive to this parameter. Further improvements in biogenic VOC emission estimates for the UK therefore remains a priority.

5.3 Non-Methane Hydrocarbons (NMVOC)

This class of organic compounds comprises the C_2-C_8 paraffins (alkanes), olefins (alkenes), acetylenes (alkynes) and aromatic hydrocarbons (arenes). They have long been recognised as the most important class for ground level ozone formation. They also comprise the largest bulk of the emissions of organic compounds from human activities. Until relatively recently, sporadic grab samples have provided the majority of information on ambient concentrations in the UK. Much of this early data was reviewed in the third PORG report (PORG 1993).

5.3.1 Hydrocarbons Monitoring Network

In the summer of 1991, with support from the Air Quality Research Programme of the Department of Environment, Transport and the Regions (DETR), hourly automatic gas chromatographic measurements of the light non-methane hydrocarbons were started in Exhibition Road, London as a prelude to more widespread monitoring. In the following year the hydrocarbon network was established. This network expanded to 1 rural and 11 urban background sites, monitoring 25 C_2-C_8 hydrocarbons on an hourly, automatic basis. It also provides on-line monitoring data for the human carcinogens, benzene and 1,3-butadiene to CEEFAX/TELETEXT. Current data on all compounds are issued hourly on the World Wide Web through the Department of Environment, Transport and the Regions home page:

http://open.gov.uk/doe/doehome.htm

All of the data collected from the network are available on the National Air Quality Information Archive established by NETCEN on behalf of the Department of Environment, Transport and the Regions:

http://www/aeat.co.uk/netcen/aqarchive/archome.html

All of the sites are illustrated in Figure 5.3 (see also Chapter 3, Tables 3.1 and 3.2). With the exception of the London UCL (Bloomsbury), which is on a roadside and the Harwell site, all the network sites have been established at urban background locations near to city centres and close to residential areas. At the London UCL site the air samples are collected approximately 4 m from the kerb-side of a busy road (Gordon Square). The Harwell instrument is at a background site in rural Oxfordshire. In practice the sites have been established at a range of locations that would reflect emissions from a variety of sources including motor vehicles and industry.

The equipment used to monitor hydrocarbons is the Chrompack VOCAIR system. The equipment makes gas chromatographic determinations at hourly intervals. The system consists of an automatic thermo-desorption/cryogenic trapping system (Auto TCT), connected to a Chrompack gas chromatograph (GC). Cooling requirements for the adsorption trap and cryofocussing traps are met with liquid nitrogen which is held in pressurised Dewar flasks at each site.

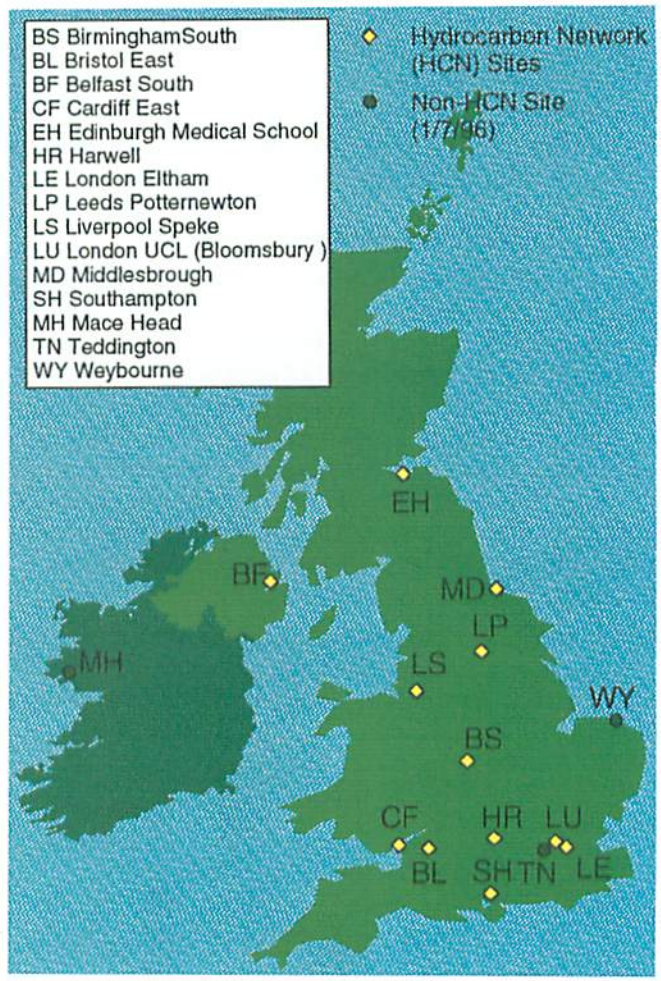

Figure 5.3 Hydrocarbon monitoring sites in the UK.

A PC installed alongside the equipment operates several software packages to collect the raw chromatogram (binary file), integrate the peaks and produces a report file. The site PC is polled each hour via modem and all files are retrieved for storage on a workstation computer.

Final quantification is through application of response factors derived from injection of certified standards, provided by the National Physical Laboratory (NPL).

It is clear that the routine operation of the network generates large numbers of hourly data values. Each site can generate in excess of 8000 chromatograms per year. The compounds routinely reported are shown in Table 5.3. These 25 compounds represent a mixture of sources from natural gas leakage, motor vehicle usage and industrial activities. All raw data are archived for future reference.

5.3.2 Hydrocarbon Network Monitoring Data

Monthly data

Ratified data from the sites are summarised in Appendix 6.1. The tables summarise data capture, monthly means, maximum and minimum hourly values. Data capture is lower for sites becoming operational during 1995. Only general observations are made on the data with specific comments on differences in the behaviour

of individual compounds within and between the measurement sites. Several factors will influence the measured concentration of these compounds including the intensity and distribution of emissions and the rate at which their chemical destruction proceeds in the atmosphere. At some sites strong local sources/releases of hydrocarbons will influence the data set. Data from all sites show month to month or seasonal variation in concentrations with highest concentrations present during the winter months, typically October to December. Minima in concentrations occur during the summertime period June to August. Diurnal patterns in concentrations are discussed in Section 3.2.2. All of the values plotted or tabulated in the following sections are based upon hourly determinations. Typically each monthly mean will be derived from in excess of 700 determinations.

Table 5.3 Compounds reported by the HCN

Standard Name	Common Name
ethane	
ethene	ethylene
propane	
propene	propylene
ethyne	acetylene
2-methyl propane	iso-butane
butane	n-butane
1-butene	
cis-2-butene	
trans-2-butene	
2-methyl butane	iso-pentane
pentane	n-pentane
1,3-butadiene	
trans-2-pentene	
cis-2-pentene	
2 methyl pentane	
3 methyl pentane	
2 methyl 1,3-butadiene	isoprene
hexane	n-hexane
heptane	n-heptane
benzene	
methylbenzene	toluene
ethylbenzene	
1,4-dimethylbenzene	p-xylene*
1,2-dimethylbenzene	o-xylene

*p-xylene is reported with m-xylene as m+p-xylene

Table A6.1.4 summarises data for Belfast. Large concentrations of propane are evident. A sudden change in propane concentration occurred during October 1994 which has been traced to a leakage from a propane gas storage facility in the area. Such tanks, which are a feature of the urban area as a result of the absence of any piped natural gas supplies to the city, hold the alternative heating fuel supplies. Natural gas is an important source of ethane leakage and when compared to other sites, the ethane concentrations in Belfast are low. The Belfast data do not show any significant diurnal variation indicating the absence of local sources. This illustrates the impact of natural gas supplies at sites on the UK mainland.

Cardiff data are summarised in Table A6.1.9. It is interesting to note the consistently high concentrations of ethane (5 to 8 ppb) at this site. These high concentrations (relative to the other sites) are most likely generated by leakage of natural gas from domestic supply pipes in the vicinity of the site. Isolated 1,3 butadiene peaks have been detected at this site, mainly in SW air flows; these may result from handling operations at Barry Docks some way to the SW of the site.

Edinburgh data are shown in Table A6.1.11. Edinburgh generally exhibits the lowest concentrations of all the sites. It is interesting to note that summertime peaks in propane, ethane and butane data are elevated; these may be associated with leakage from gas handling facilities in the region. Propene concentrations in Edinburgh are very consistent and show little seasonal variation.

The London background data for Eltham are summarised in Table A6.1.3. Acetylene and ethene are present in the highest concentrations at this site. The relatively smooth month to month behaviour probably reflects the predominance of urban motor vehicle usage as the main source of hydrocarbons. Isoprene may be enhanced somewhat possibly reflecting the presence of trees in the vicinity of the site. At all the sites isoprene exhibits behaviour similar to the other compounds. It is possible that in addition to the natural sources of isoprene (Section 5.2.2) there is an additional source from the combustion of fuel.

Middlesbrough is the longest running network site. The data are summarised in Table A6.1.12. Middlesbrough exhibits high concentrations of several compounds some of which are likely to originate from local industrial sources: acetylene, propane and butanes show notable high concentrations and local non motor-vehicle sources of 1,3-butadiene are evident.

London UCL is situated at a roadside, in contrast to the other sites which are all at urban background locations. The emissions of hydrocarbons at this site are dominated by motor vehicles; the data are summarised in Table A6.1.5. Acetylene shows the highest concentrations as might be expected with motor vehicle combustion being its sole source.

Acetylene and ethane are the most abundant species at Birmingham (Table A6.1.8). The data for Leeds, Liverpool and Southampton sites which commenced data collection during 1995, are shown in Tables A6.1.10, A6.1.6 and A6.1.7 respectively. The data for the (rural) site at Harwell are summarised in Table A6.1.1.

Appendix 6.2 summarises an extended series of analyses of grab samples collected at Teddington by the National Physical Laboratory. This time series includes data on 39 individual hydrocarbon species in addition to methane.

Light hydrocarbons, ethane and propane

In this section, the measured concentrations of the light hydrocarbons ethane and propane from the 10 urban background sites are analysed in some detail. The measurements are assessed against comparable measurements made at the urban roadside site. London UCL, and the rural site (Harwell) and with literature measurements covering north west Europe from the Netherlands northwards to Finland.

Figure 5.4 shows the annual mean diurnal curves for ethane for 1995 at the 10 urban background sites, urban

roadside and rural site; Figure 5.5 shows those for the summer period, April - September and Figure 5.6 for the winter period, January - March and October to December. These curves are characterised by increasing concentrations during the early hours of the morning, decreasing concentrations during the mid morning and a mid afternoon minimum. Concentrations then increase during late afternoon and the evening.

During wintertime, ethane levels are generally higher during night-time and the midday trough is significantly narrower in time compared with summertime. The wintertime midday trough is shallowest in Liverpool and levels are highest during this season at Cardiff. During summertime, the midday minimum ethane concentrations are virtually independent of site, whether urban or rural, roadside or background, with the exception of Cardiff.

This behaviour, as revealed in the diurnal curves for ethane is interpreted as due largely to changes in atmospheric stability and mixing in the lowest layers of the atmosphere and their influence on a ground level source. The main urban source of ethane is natural gas leakage from transmission and distribution pipes buried below ground. There is no evidence to suggest that this source is anything other than constant in magnitude from day to day, except under conditions of fracture. Ethane concentrations from natural gas leakage are expected to follow changes in boundary layer depth and atmospheric stability. Boundary layers are generally lowest at night and stability greatest, leading to highest ethane concentrations. In the mid afternoon boundary layers are generally greatest in depth, mixing and dispersion process most efficient and surface layers are well connected to a considerable depth of the atmosphere.

If natural gas leakage were the only source of ethane, concentrations would be expected to fall to low values during the middle of the afternoon. Although urban mid-afternoon values are lowest, they certainly are not negligible. Indeed urban values approach rural values closely during mid-afternoon, suggesting the presence of a tropospheric ethane background level upon which the urban natural gas leakage source is superimposed.

Figure 5.7 shows the mid-afternoon ethane concentrations recorded at various UK urban sites compared with rural measurements made at several sites across north and west Europe. From this it is clear that there is indeed a tropospheric ethane background contribution to the urban ethane levels measured in the UK and that this amounts to about 2-3 ppb during winter and 1-2 ppb during summer.

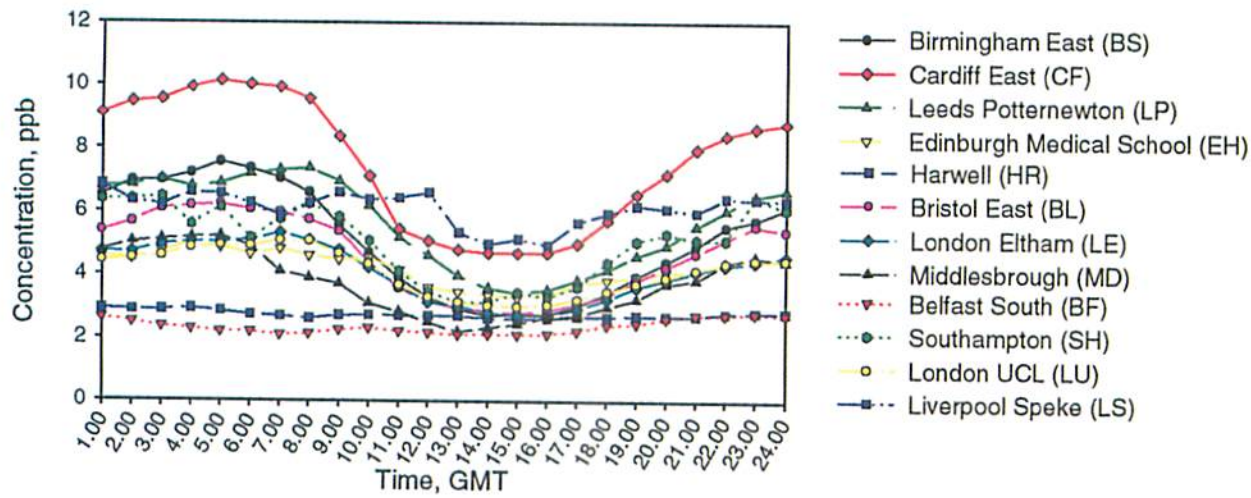

Figure 5.4 Annual mean diurnal ethane concentrations at HCN sites for 1995.

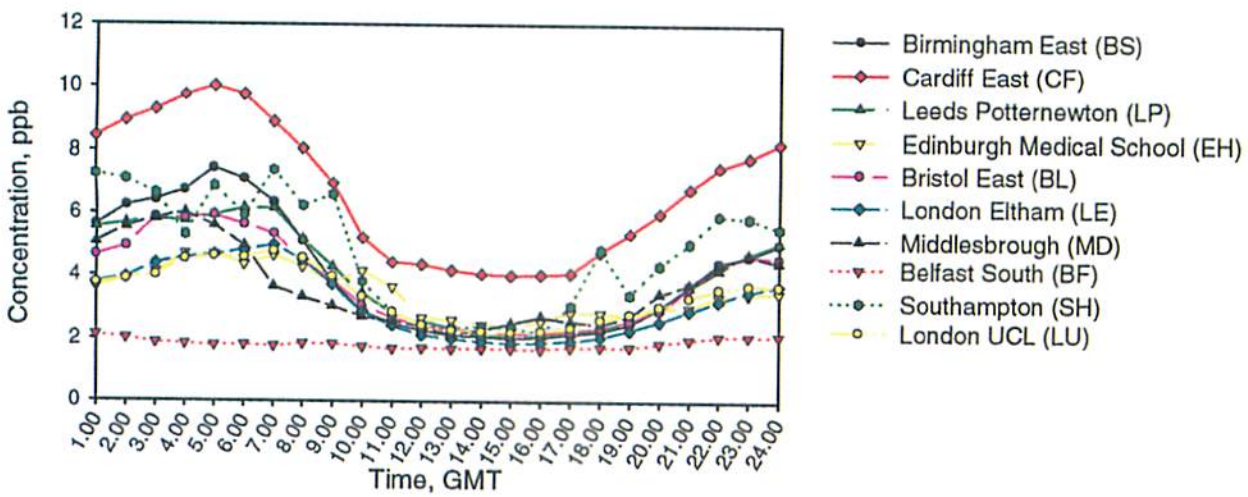

Figure 5.5 Summer (Apr-Sept) mean diurnal ethane concentrations at HCN sites for 1995.

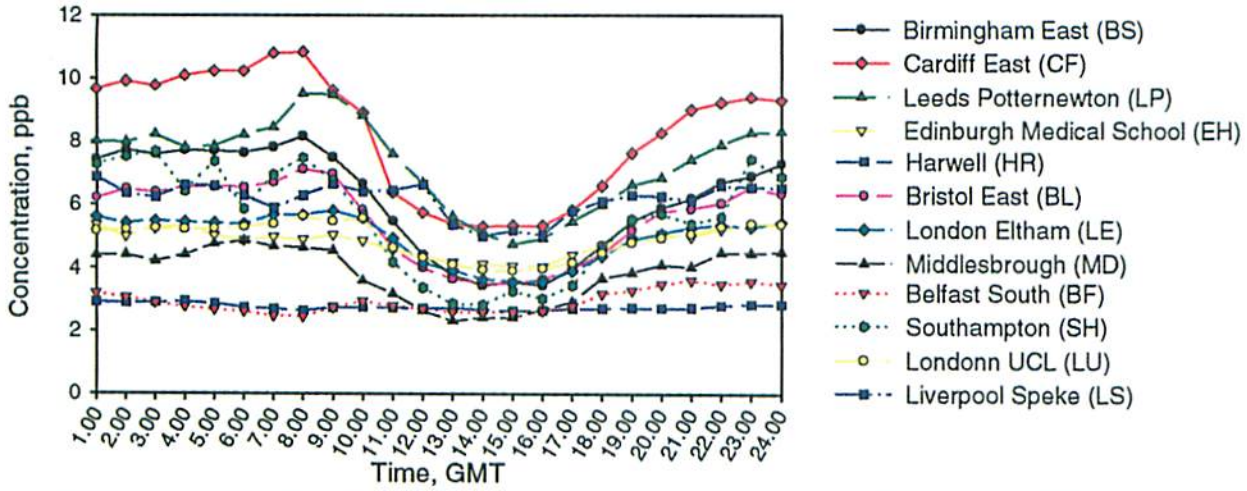

Figure 5.6 Winter (Jan-Mar, Oct-Dec) mean diurnal ethane concentrations at HCN sites for 1995.

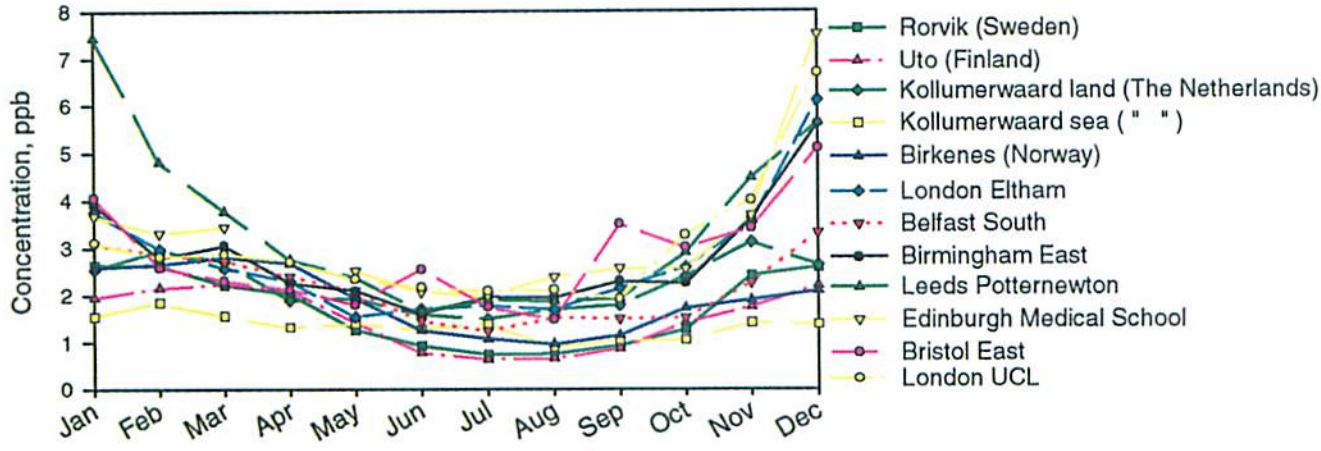

Figure 5.7 Mid-afternoon (1500) mean ethane concentrations at European and UK sites for 1995.

Table 5.4 shows the mean (0000 - 0600 hours) and mid-afternoon (1500 hours) ethane concentrations measured during summertime and wintertime at each UK site. This table shows that natural gas leakage is a significant source of ethane at all the sites except for Harwell, the rural site, and Belfast, the urban site is the only city surveyed in this study without a natural gas distribution network. Natural gas leakage seems to be most significant in Cardiff and least significant in Middlesbrough in winter time. In summertime the night time mean concentrations are significantly lower since dispersion conditions are generally better in urban areas in summer compared to winter. Cardiff again has the most significant source, with Edinburgh and London showing the least significant sources.

With ethane there is no evidence of a traffic-related source at any site, as although the diurnal curves change with season the rush-hour timings remain unaltered and the curves show no systematic weekend-weekday differences.

The estimated ethane emission rates from natural gas leakage in each urban centre during April - September 1995 have been calculated from the London UCL night-time - mid-afternoon concentration difference. Belfast has close to an order of magnitude lower natural gas leakage source to the strength of London. That this Belfast source strength is not zero reflects use or leakage of LPG (Liquid Propane Gas). The two independent estimates for London from the London Eltham and London UCL agree within the likely error bars. The other urban centres then rank, in ascending order:

Edinburgh < London < Middlesbrough < Bristol < Southampton < Leeds < Birmingham < Cardiff

Figure 5.8 shows the mean diurnal curves for propane for 1995 for the 10 urban background sites, the urban roadside site and the rural site, with Figure 5.9 covering the summertime period, April - September and Figure 5.10 for the winter period, January - March and October - December. These mean diurnal curves show more variability than those for ethane,although similar trends with the lowest concentrations in mid-afternoon and highest concentrations in the early morning are observed, particularly during the summertime, in an analogous manner as for ethane.

The mean summertime annual curves for propane at seven sites: London Eltham, Birmingham, Bristol, Leeds, London UCL, Cardiff and Edinburgh are all highly consistent with each other. Mid-afternoon summertime

levels at 1500 hours lie in the range 0.8 - 1.8 ppb and are somewhat higher than the northern hemisphere baseline levels of 0.2 - 0.4 ppb measured at three remote rural sites in Northwest Europe, see Figure 5.11.

Night-time propane levels are considerably elevated above summertime mid-afternoon levels suggesting the presence of a surface urban source which is assumed to be natural gas leakage. Table 5.4 summarises the mean night-time and mid-afternoon propane levels found during the summertime and wintertime at all the sites. The night-time propane source appears to be weakest at London Eltham and strongest at Birmingham, considering the seven sites that show reasonably consistent behaviour.

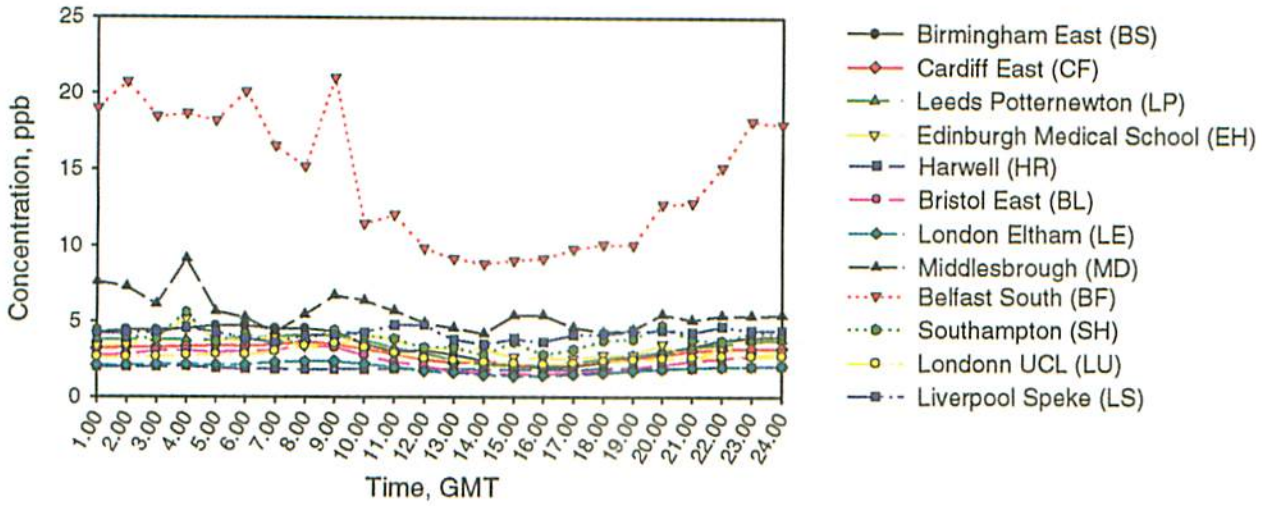

Figure 5.8 Annual mean diurnal propane concentrations at HCN sites for 1995.

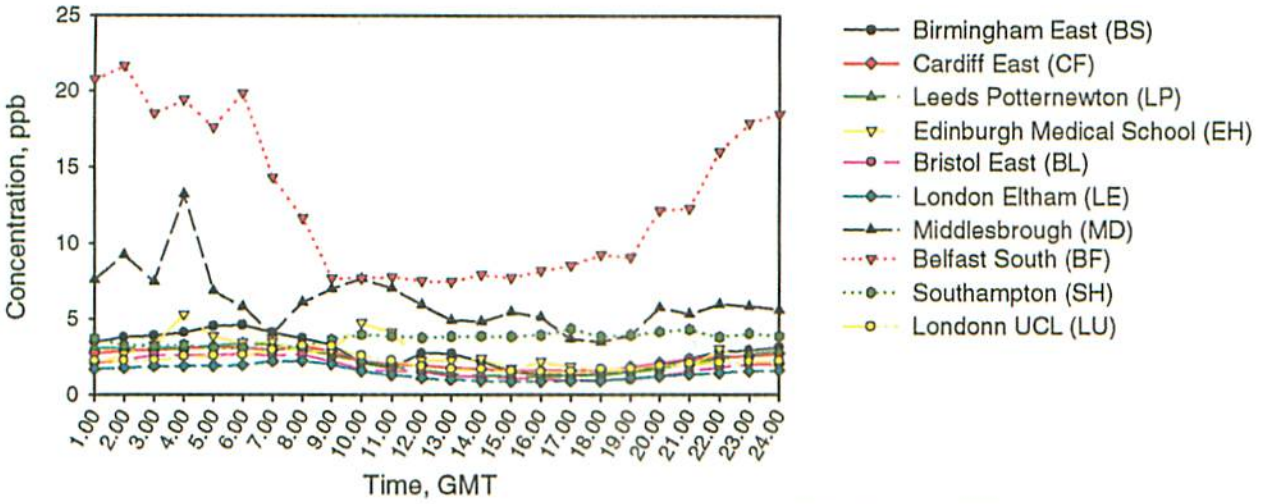

Figure 5.9 Summer (Apr-Sept) mean diurnal propane concentrations at HCN sites for 1995.

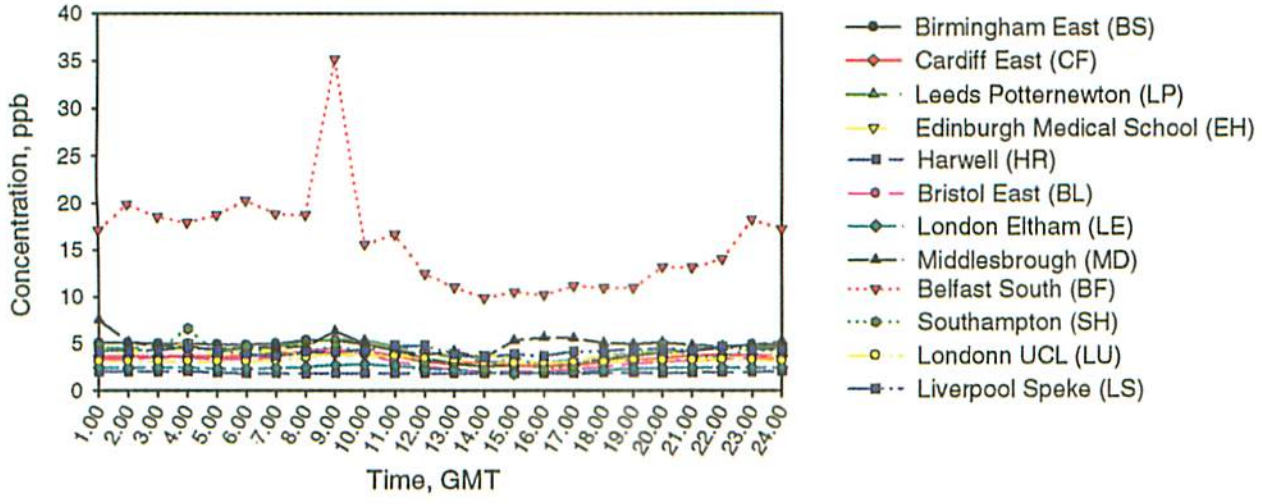

Figure 5.10 Winter (Jan-Mar, Oct-Dec) mean diurnal propane concentrations at HCN sites for 1995.

Table 5.4 Mean ethane and propane concentrations for all sites during the winter and summer periods of 1995 for the mid-afternoon (1500) and nightime (0000 - 0600).

	Winter		Summer	
Ethane	**1500**	**0000-0600**	**1500**	**0000-0600**
Birmingham	3.55	7.58	2.03	6.39
Cardiff	5.34	9.90	4.03	9.21
Leeds	4.74	8.05	2.09	5.71
Edinburgh	4.07	5.18	2.37	4.14
Harwel	2.63	2.87	-	-
Bristol	3.51	6.43	2.17	5.36
London Eltham	3.56	5.45	1.88	4.28
Middlesbrough	2.42	4.50	2.50	5.51
Belfast	2.60	2.96	1.70	1.95
Southampton	3.52	5.95	3.19	6.55
London Bloomsbury (UCL)	3.90	5.25	2.22	4.17
Liverpool	5.16	6.47	-	-
Propane	**1500**	**0000-0600**	**1500**	**0000-0600**
Birmingham	2.67	4.97	1.53	3.96
Cardiff	2.59	3.66	1.59	2.93
Leeds	2.93	4.49	1.23	3.14
Edinburgh	3.44	4.25	1.77	3.24
Harwell	1.84	1.99	-	-
Bristol	2.03	3.45	1.15	2.46
London Eltham	1.88	2.41	0.90	1.83
Middlesbrough	5.35	5.23	5.50	8.02
Belfast	10.57	18.45	7.71	19.58
Southampton	3.60	4.71	3.87	3.38
London Bloomsbury (UCL)	2.99	3.15	1.59	2.42
Liverpool	3.88	4.29	-	-

Note: Winter ≡ (Jan - Mar, Oct - Nov), Summer ≡ Apr - Sep.

Average diurnal curves for propane in the wintertime show evidence for a mid-afternoon minimum which is much less pronounced compared with that for ethane. This mid-afternoon baseline value of 2-3 ppb is considerably higher than the summertime value and is consistent with a much stronger seasonal cycle reported for propane compared with ethane.

Summertime propane levels are particularly high for Belfast as indeed are the wintertime levels. This is believed to be due to leakage from LPG storage, a local phenomenon (see above). Propane levels at the Middlesbrough site are particularly high throughout the summertime, although with the same diurnal variation as other sites. Interestingly, winter-time propane levels are lower than summertime levels. Southampton summertime propane levels show little diurnal variation presumably due to the shortness of the record.

The behaviour shown for propane at the seven self-consistent sites: London Eltham, Birmingham, Bristol, Leeds, London UCL, Cardiff and Edinburgh, is interpreted as due largely to natural gas leakage as the dominant propane source. Propane concentrations are expected to follow changes in boundary layer depth and atmospheric stability in exactly the same manner as with ethane.

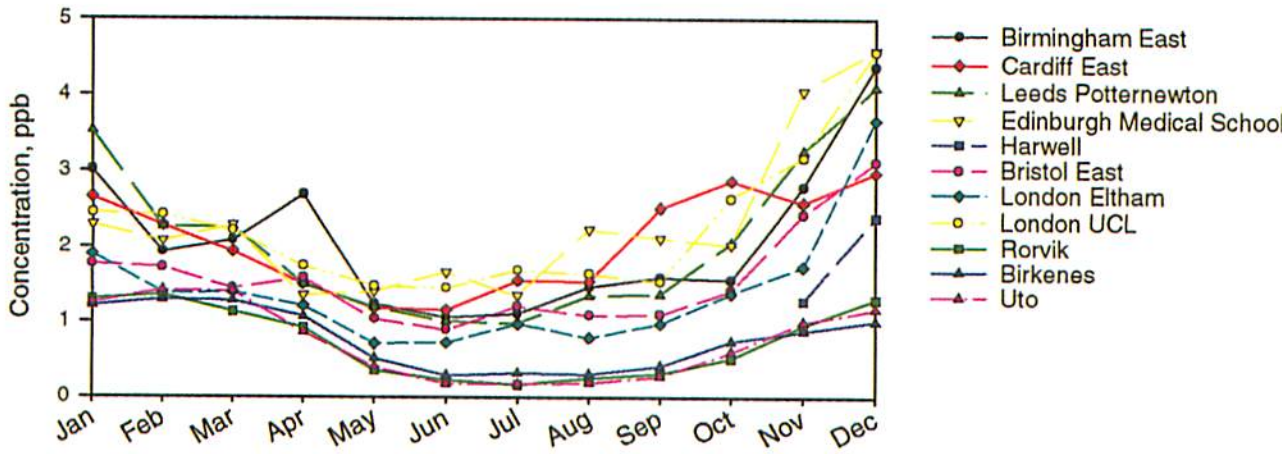

Figure 5.11 Mid-afternoon (1500) annual propane concentrations at European and UK sites for 1995.

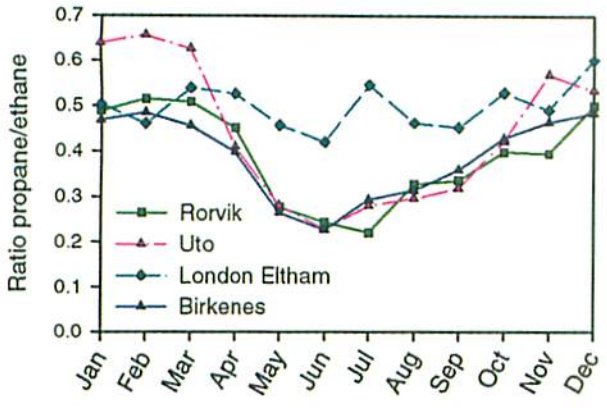

Figure 5.12 Mid-afternoon (1500) ratios of propane to ethane at northern hemisphere background sites and London Eltham.

Figure 5.12 plots the ratio of the mid-afternoon concentrations of propane to ethane at the northern hemisphere baseline sites compared with London Eltham. The ratios agree well during the winter but diverge increasingly during the summertime. The summertime propane levels at London Eltham are therefore not derived from the northern hemisphere baseline as they are at the remote rural sites and another source must be involved. It is concluded that throughout the year, natural gas leakage is the dominant source of propane measured at the London Eltham site and by implication the other self-consistent sites.

Propane therefore differs from ethane at the UK urban sites, since the northern hemisphere baseline contributes significantly to the latter and not to the former during summertime. This is because of the shorter atmospheric lifetime for propane which dramatically reduces its baseline concentrations. By implication, the wintertime ethane and propane concentrations at the remote, rural sites may be influenced by man made sources such as natural gas leakage.

Ethane and propane concentrations are generally closely correlated, this is illustrated in Figure 5.13, with the notable exception of Middlesbrough where local industrial emissions influence the ratio.

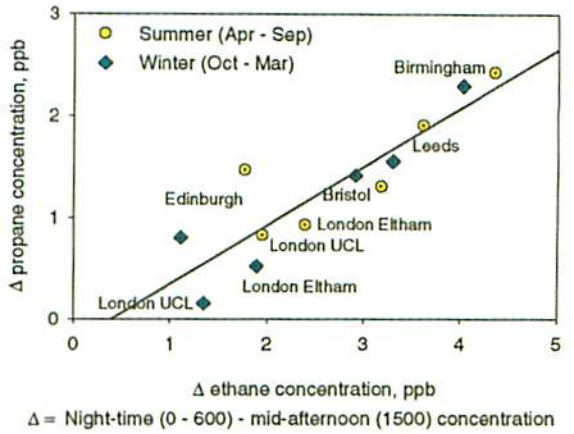

Figure 5.14 Difference between mid-afternoon and night-time concentrations of propane and ethane at HCN sites during summer and winter periods of 1995.

The by-volume propane to ethane ratio for natural gas leakage can be derived from the data in Figure 5.14, in which night-time mid-afternoon concentration differences from Table 5.4 are plotted out for ethane and propane. The slope of this plot corresponds to a concentration ratio of 0.58. This ratio is significantly different to the propane to ethane concentration ratio of around 2, apparent from data reported in the National Atmospheric Emission inventory. The difference in the ratio is consistent with the mean reactivity of these compounds in the atmosphere, where the rate of destruction of propane is about four times greater than that of ethane.

Plots of ppbC for network sites

Figure 5.15a to 5.15i present the total hydrocarbon concentrations at each site as ppbC (ppb x number of carbon atoms) on a monthly mean basis and split into six categories C_2 + C_3, C_4, C_5, C_6, C_7 and C_8 compounds.

The C_2 + C_3 compounds tend to dominate largely because of the contribution of ethane. The C_2 + C_3 category can display a strong seasonal variation, for example at Belfast (Figure 5.15a) contributing 30 to 40% during the winter period and 20 to 25% during the

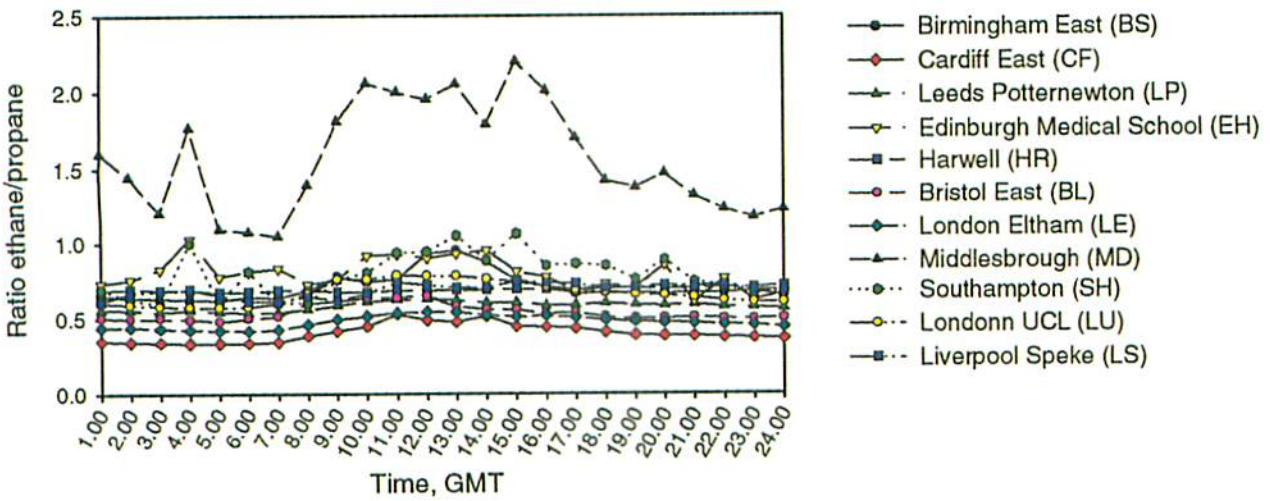

Figure 5.13 Ratio of propane/ethane annual mean diurnal cycles at HCN sites for 1995.

summer period. Similar seasonality is apparent at London Eltham, London UCL and Middlesbrough (Figures 5.15b to d). Other sites show reduced month to month variation for example, Cardiff (Figure 5.15e), where ethane concentrations where the highest.

Figure 5.16 summarises data for all sites, this shows the annual mean concentrations as a ppbC plot. It is evident that Edinburgh is the site with the lowest hydrocarbon concentrations, Belfast, Bristol, London Eltham and Birmingham are all very similar. Cardiff appears to show elevated C_4, C_5, and C_6 species. Middlesbrough and London UCL (roadside) site show the highest concentrations. At the Edinburgh site the $C_2 + C_3$ is the major category because of the relatively large contribution made by ethane. Across the other sites the $C_2 + C_3$ category is reasonably consistent (allowing for enhanced propane at Belfast and probably reduced ethane sensitivity at Bristol). The other categories increase in proportion to the $C_2 + C_3$ total with Middlesbrough and London UCL showing substantial enhancements in the C_4 through to C_8 region.

Local episodes

It is evident from the data presented above that several factors combine to generate seasonal and diurnal patterns within the measurement data. It is clearly important to understand these variations in terms of the factors influencing the formation of photochemical oxidants and, when the compound is of importance because of its toxicity towards people, the exposure of the population.

When the data sets are examined well-defined episodes of elevated concentrations may be detected. These episodes broadly are of two types: the first are typically of 24 to 48 hours duration and tend to reverse the expected diurnal patterns discussed above. These episodes tend to be driven by the effects of meteorology. The second are shorter-lived, lasting up to several hours and typically originate from emissions from local industrial point sources.

An example of the first type is illustrated in Figure 5.17. This plot shows data collected at Birmingham over several days during December 1994. The plot shows benzene along with data on several inorganic pollutants. Concentrations of all species except SO_2 deviate from the 'normal' urban values in a highly correlated fashion and peak during the night-time period of 23rd December. The increases in concentrations are linked to the emission of pollutants and to the cooling and contracting of the boundary layer which, at the time of the peak concentrations, may have been as little as several tens of metres in depth. The absence of effective dispersion within this shallow layer will allow emitted pollutants to accumulate. Emissions at the Birmingham site are strongly influenced by motor vehicles; the low levels of SO_2 reflect motor vehicles as only a weak source. The net result is a prolonged exposure of the population to elevated concentrations over the night-time period. This type of episode would be expected to occur several times at any one site during the autumn/winter periods and the effect can extend across several sites because of the scale of the prevailing meteorological conditions.

The second type of episode is illustrated by data collected at the Middlesbrough site for 1,3-butadiene. Figure 5.18 illustrates hourly data collected during the period 31st July to 2nd August 1995. Typical urban concentrations of 1,3-butadiene are in the range 0.2-0.4 ppb; during the afternoon of 31st July 1995 concentrations climbed to an unprecedented high level (peak 74 ppb). The episode lasted for several hours with normal 'ambient' levels restored in the early morning hours. The 1,3-butadiene was clearly elevated, relative to other VOCs, beyond the levels expected from motor vehicle emissions. The emission was eventually tracked to an "industrial process" involving cleaning of storage tanks on sea-going tankers. It is estimated that 7 t of 1,3-butadiene were released during this incident. 1,3-butadiene is highly reactive and has a high photochemical ozone creation potential (Chapter 2), with the release of such massive amounts this type of event will undoubtedly have an impact on ozone formation downwind of the site. Of equal, if not greater concern, is the impact of such releases upon the local population. 1,3-butadiene is a carcinogen for which the UK has set an air quality standard (as described below).

Trends in urban VOC data

Probably the main interest in trends in urban VOC data relates to the carcinogenic compounds, benzene and 1,3-butadiene for which the UK has recommended air quality standards (EPAQS, 1994a,b). The standards were recommended in terms of a rolling annual mean (RAM) to take account of the cumulative nature of the impact of carcinogens on human health and are now an integral part of the UK Nation Air Quality Strategy (DoE, 1997). In the case of benzene the recommendation was for a RAM of 5 ppb and for 1,3-butadiene a RAM of 1 ppb.

Rolling annual mean data for the network sites are illustrated in Figure 5.19 for benzene. In order to simplify plotting of the RAM (which is calculated for every hour of the year) the RAM value at the end of each week is shown for the periods the sites have been collecting data. Each value represents the mean for the previous 12 months; thus the data for the London roadside site begin in January 1993 and the whole plot is based upon over 30000 hourly measurements. At any one point, the rolling annual mean is affected by all values within the 12 month time frame. This generates the trends in the RAM and represents a measure of the dose to the population during the previous 12 months.

The RAMs display a considerable variation form site to site although none have breached the Expert Panel on Air Quality Standards (EPAQS) recommended level of 5 ppb. The Leeds, Southampton and Liverpool sites were established relatively recently and the system at the Harwell site has been used for network development and testing for a number of periods and so has not operated in a continuous manner until relatively recently. As a result there are not yet enough data to show any clear trend in the RAMs for benzene and 1,3-butadiene at these sites.

Considering first the benzene data. The plots for Belfast and Cardiff demonstrate similar patterns.

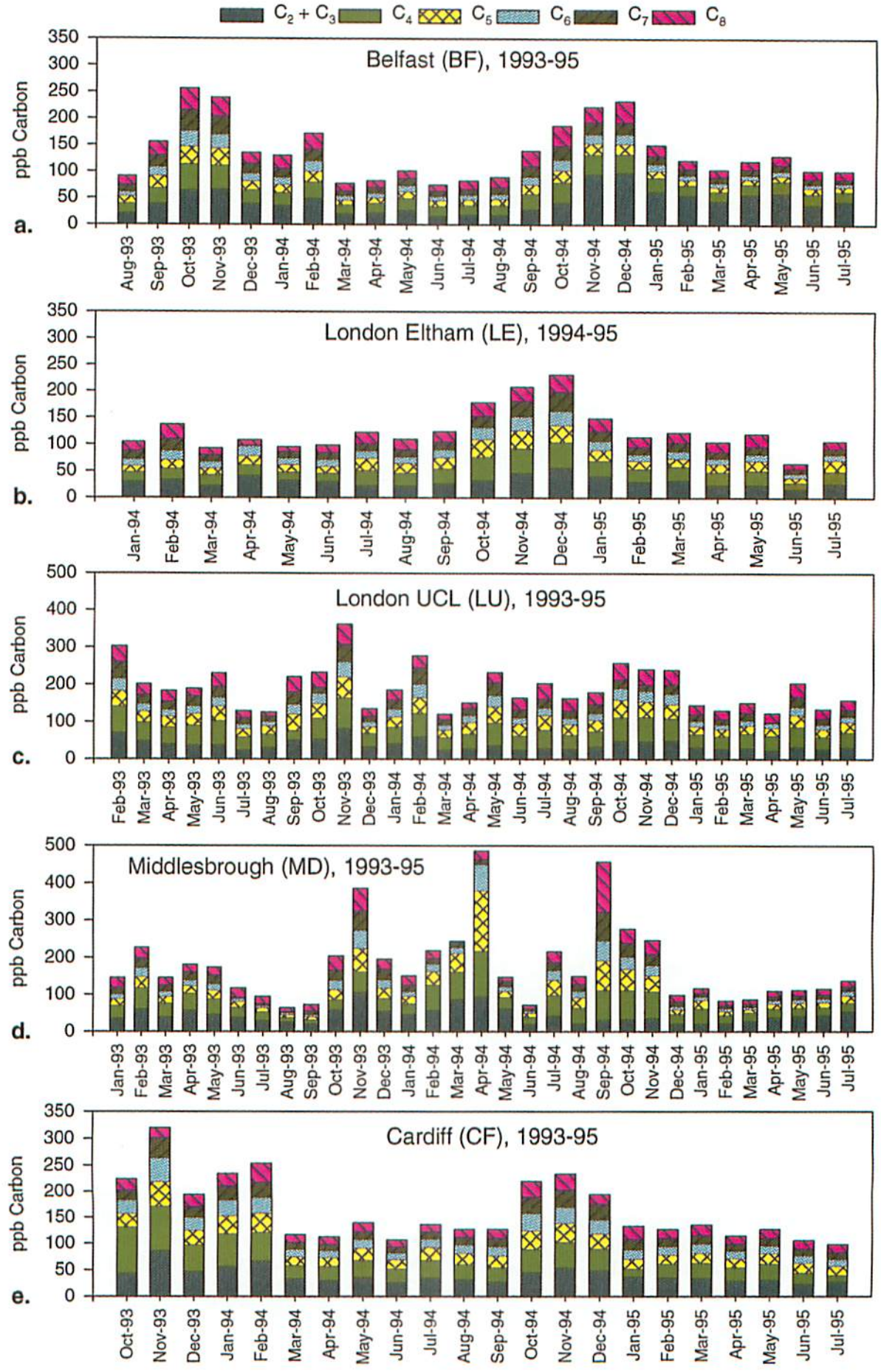

Figure 5.15 a to e Monthly mean total hydrocarbon concentrations at HCN sites, split into six categories: C_2+C_3, C4, C_5, C_6, C_7 and C_8 compounds.

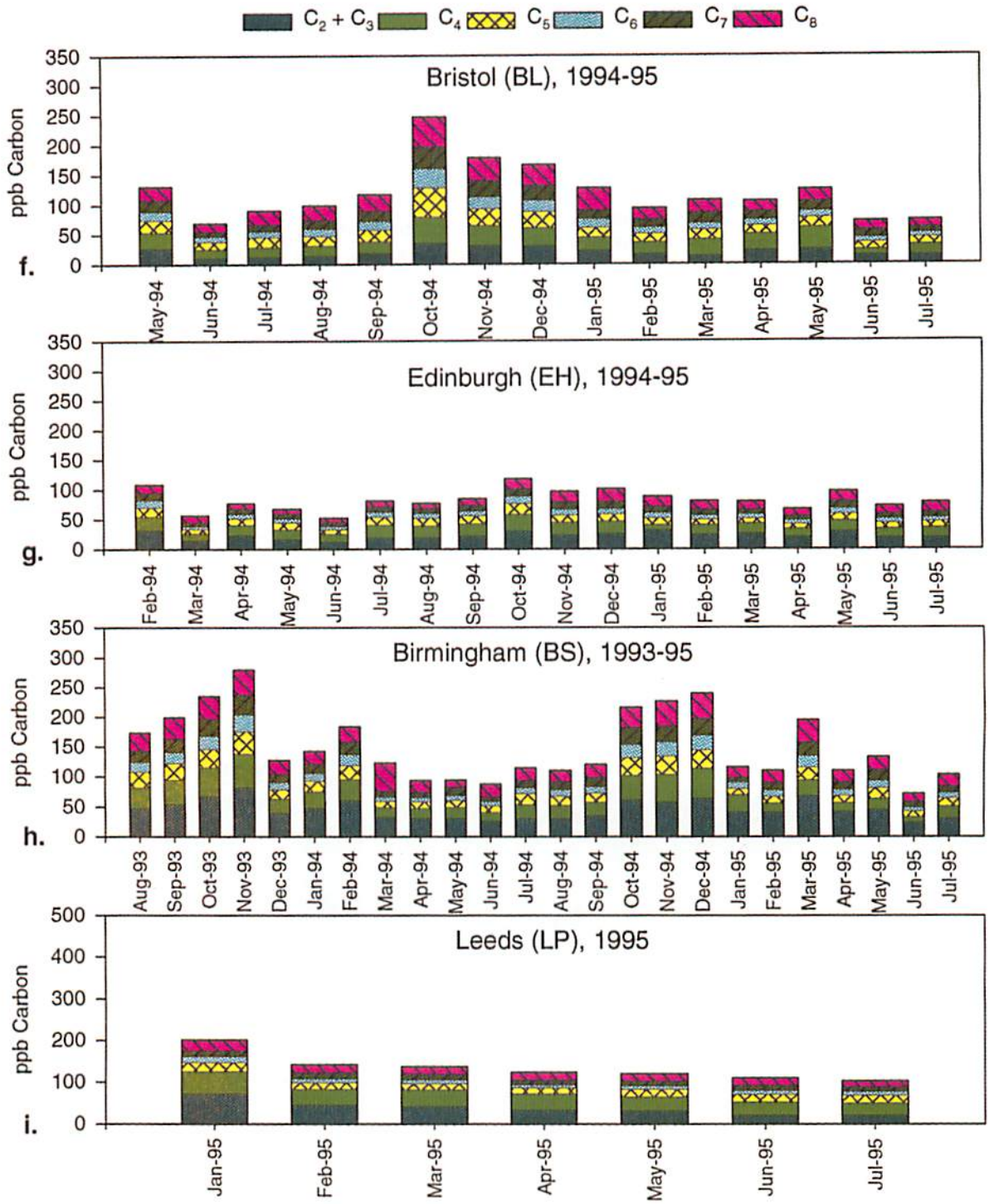

Figure 5.15 f to i Monthly mean total hydrocarbon concentrations at HCN sites, split into six categories: C_2+C_3, C_4, C_5, C_6, C_7 and C_8 compounds.

The values for Belfast show a decline in levels from the middle of 1994 up to the end of 1995. The levels then show a small rise, levelling out to the present value. The reduction at Belfast over the 2 year period 1994 - 1996 is approximately 20%. The reduction over the same period for the Cardiff data is approximately 15% although there appears to be a slightly greater amplitude to the annual variation.

The plots for Birmingham and Edinburgh are very similar both displaying relatively constant values for the RAMs. The value for Birmingham is about 1 ppb and for Edinburgh 0.7 ppb. Edinburgh is the only urban site in the network to be constantly below 1 ppb.

The value for the London Eltham site dropped by about 20% over the first 6 months of operation and then remained relatively constant at about 1 ppb. Over the same time period this site is very similar to the plots for the Edinburgh and Middlesbrough sites.

The plot of the London UCL RAM exhibits a steady drop over the first 12 months then remains fairly constant

over the next 9 months. The RAM then increases over a 3 month period before remaining relatively stable until a slight drop over the final 2 months. The pattern at London Eltham is similar to that of UCL although the amplitude of change is significantly less at the Eltham site. This may be due to the fact that the Eltham site is an urban background site and UCL is positioned at a roadside.

The monitoring site at Middlesbrough shows some of the most interesting data as there is comparatively large variation over time on a baseline that marginally decreases (<5%). The reason for this variation in levels is most probably due to the influence of local non-motor vehicle emissions.

The only site that has shown an increase in RAM levels since installation is Bristol. There has been an increase of approximately 15% from early 1995 to mid-1996 with a slight decrease in the final 2 to 3 months. This could be attributed to either local sources or meteorology. The daily variations at Bristol are similar to those at Cardiff and so it has been assumed that the proximity of the 2 cities and consequent similarities in meteorology might account for the similarities in daily observations. The observed difference in the long term trend is therefore less likely to be due to meteorology. However, there are no known local sources of benzene that might help explain the observed trend.

Data are not shown for 1,3-butadiene which exhibits a very similar pattern of behaviour to that of benzene. This might be expected given the dominant effect of motor vehicle emissions on VOC concentrations in urban areas. This is with the notable exception of Middlesbrough where there are significant non motor vehicle sources of benzene and 1,3-butadiene. Generally local, non motor vehicle emissions of these compounds do not distort the annual statistics; however, the massive release of 1,3-butadiene discussed above did distort the trend. This incident will elevate the RAM for a period of twelve months. The RAM for Middlesbrough (and all the other sites) is currently well below the 1 ppb recommended standard, however, there must be concern for populations located downwind of such sources, where exposure may be more frequent.

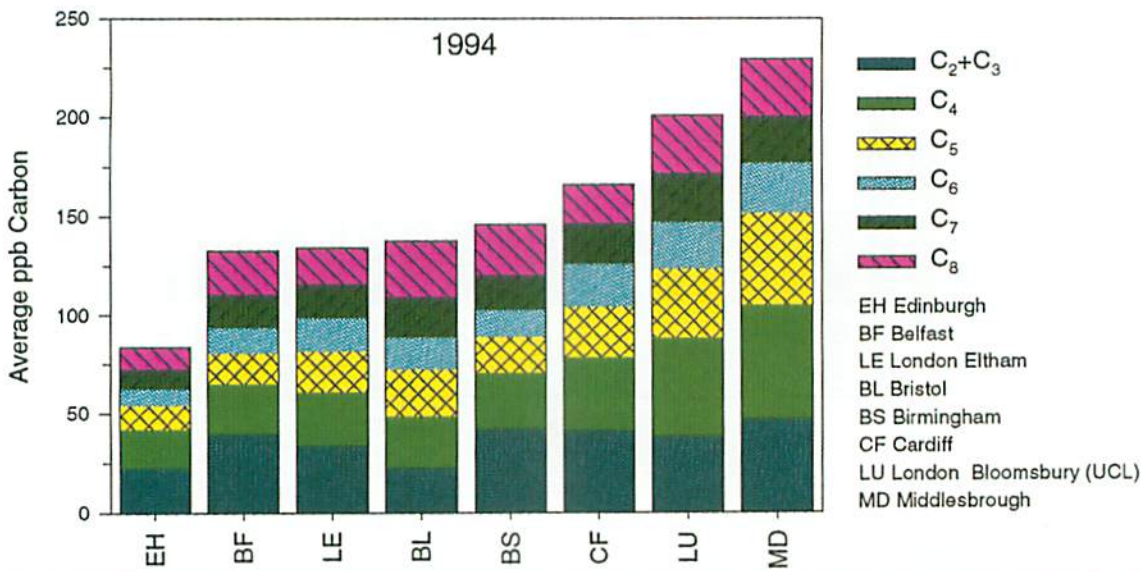

Figure 5.16 1994 mean total hydrocarbon concentrations at HCN sites, split into six categories: C_2+C_3, C_4, C_5, C_6, C_7 and C_8 compounds.

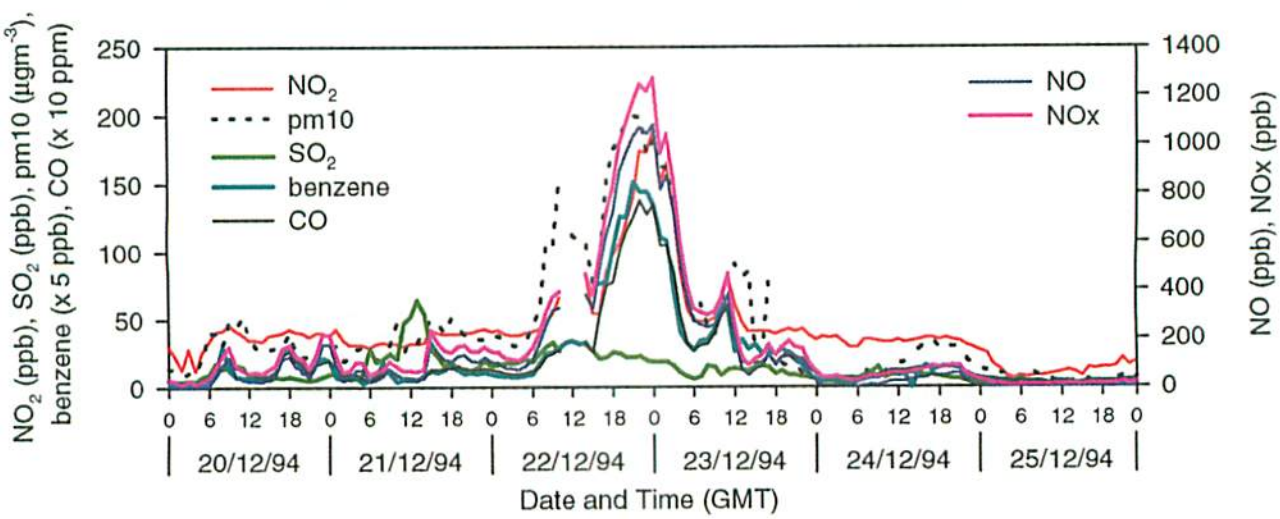

Figure 5.17 Concentrations of NO_2, PM_{10}, SO_2, benzene, CO, NO and NO_x at Birmingham East during a pollution episode, 20/12/94 to 25/12/94.

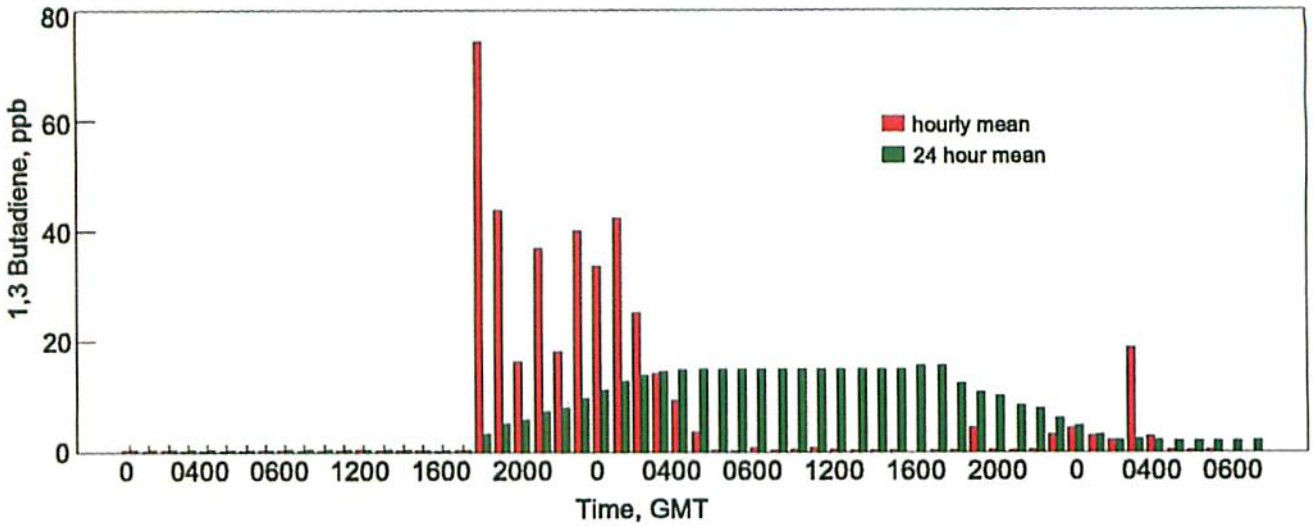

Figure 5.18 Hourly and 24 hour mean 1,3 butadiene concentration at Middlesbrough during a pollution episode, 31/7/95 to 2/8/95.

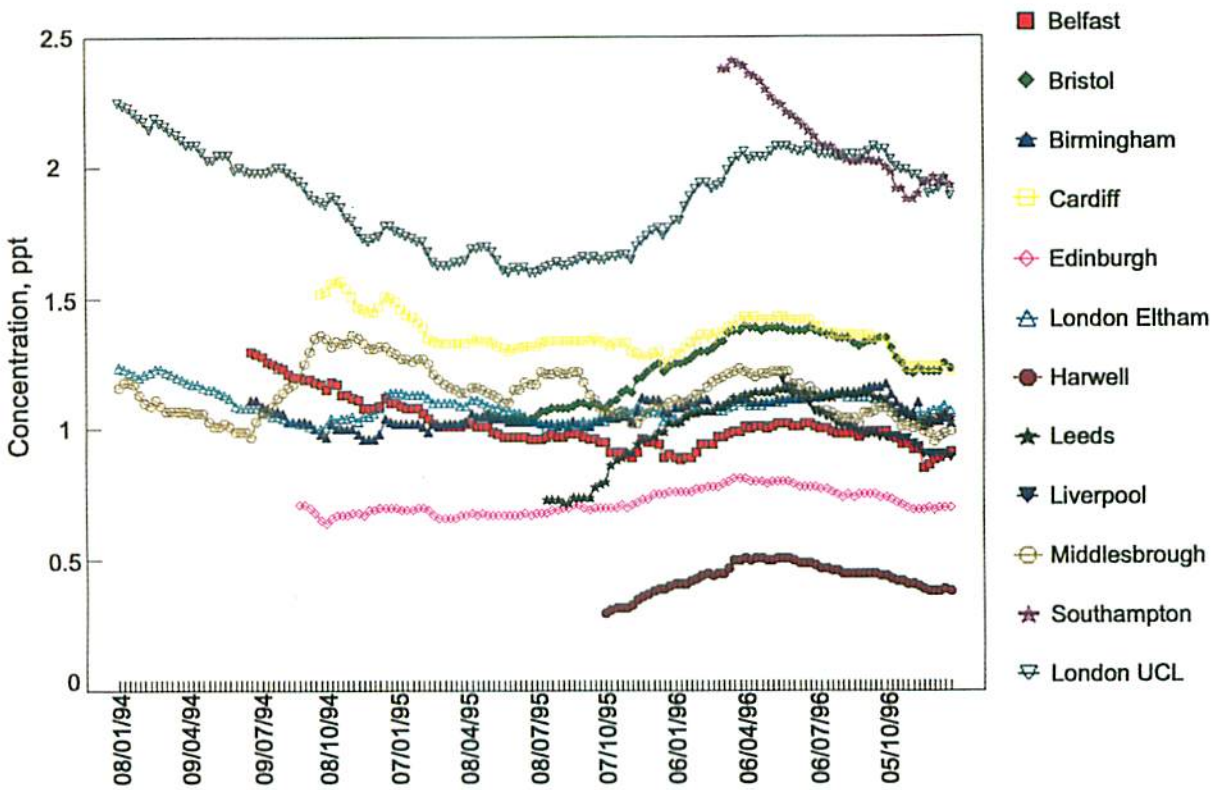

Figure 5.19 Rolling annual means (RAMs) for benzene at HCN sites.

5.4 Comparison of Emissions Inventories with Measurement Data for Light Hydrocarbons

Policy development for regional scale ozone formation in Europe has relied on photochemical models. These complex photochemical models are for the large part driven by the emission inventories and have not been constrained by the availability or the lack of hydrocarbon measurements. In this section, the hydrocarbon monitoring network data are used to ascertain whether there is any broad consistency between the emission inventories used to drive the models and the hydrocarbon network data which report the hydrocarbon loadings actually observed in the ambient atmosphere.

5.4.1 Roadside Studies

In the first type of study, air quality measurements made in environments heavily influenced by one particular emission source can be used to verify the emission factors for that source in the national emission inventory, using simple atmospheric dispersion models. Kerbside measurements can be used to verify motor vehicle emission factors and such a study has been performed using the eighteen months of measurements made by

Table 5.5 A comparison of the vehicle emission factors determined in this study from the observed air pollution concentrations and those measured on-board in petrol-engined motor vehicles on the road under typical urban driving conditions.

species	Vehicle emission factor mg/km	
	Kerbside Study (d)	On-board (b,c)
carbon monoxide	23400-30200	21400
NO_x	1788-1997	1740-2270
methane	(a)	93.4-172.78
ethane	< 5	26.25-30
propane	(a)	3.8-7.8
n-butane	185-265	91.4-130.08
i-butane	108-150	36.7-65.66
n-pentane	36-64	66.2-58.73
i-pentane	127-217	169.09
ethylene	119-162	166.7-211.94
propylene	94-144	87.6-95.29
1-butene	12-18	16.1-16.96
cisbut-2-ene	14-24	8.22
transbut-2-ene	28-60	43.4-39.30
1,3-butadiene	16-25	34.3
acetylene	249-338	163-182
benzene	90-150	116.2-195.58
toluene	138-241	316.9-453.48
o-xylene	26-49	103.8-172.19
m+p-xylene	77-137	236.7-427.38
ethylbenzene	20-39	62.4-134.99

Notes:
a. no detectable influence of traffic sources on diurnal variation.
b. Bailey and Parkes (1993).
c. Bailey, Gunary, Schmidl and Williams (1990).
d. Derwent *et al* (1995).

Field *et al* (1994) in Exhibition Road, London. Using simple dispersion models and traffic count data, the hydrocarbon measurement data can be worked back to obtain hydrocarbon emission factors for motor traffic (Derwent *et al* 1995). The application of this study type is limited by the availability of kerbside measurements in streets with heavy traffic flow.

Figure 5.20 illustrates the typical mean diurnal curves which have been observed in Exhibition Road, London immediately adjacent to a busy road where concentrations will be greater than at urban background locations. By fitting simple dispersion models for the urban background and local vehicle traffic contributions, it is possible to derive emission factors from both the observed morning and evening peak concentrations.

Table 5.5 shows the motor vehicle emission factors required to account for the ambient air quality and those measured on-board in the exhausts of petrol-engined vehicles and used in compiling emission inventories. For many hydrocarbons, there is a good level of agreement between the two sets of emission factors. For some, however, there is a considerable level of disagreement.

For the major vehicle-derived C_2 hydrocarbons, ethylene (ethene) and acetylene (ethyne) it appears that the on-board exhaust emission factors underestimate those required to explain the air quality measurements. For the C_4 and C_5 alkanes, the exhaust emission factors underestimate those derived from the measurements because of the important evaporative emissions of these compounds. For the aromatic compounds, the on-board exhaust measurements appear to overestimate the emissions required to explain observed air quality.

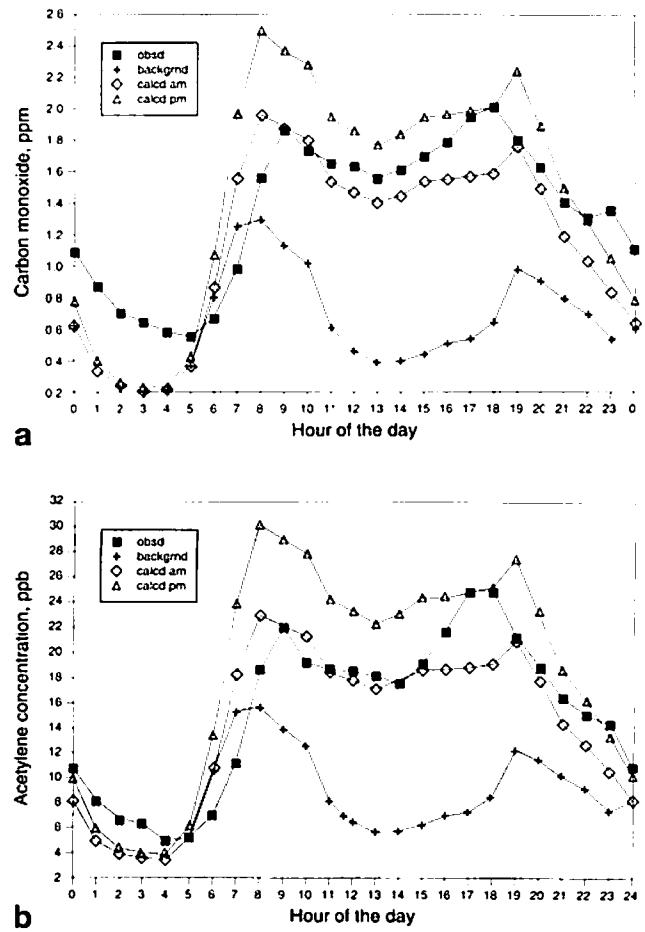

Figure 5.20 Typical mean diurnal concentration curves for (a) carbon monoxide and (b) acetylene (ethyne) measured at Exhibition Road, London.

Such comparisons allow a vital check on the vehicle exhaust emission factors required for the compilation of the emission inventories. They provide important confirmation that vehicle exhaust are the major sources of the human carcinogens, benzene and 1,3-butadiene.

5.4.2 Urban Background Studies

Ethane is an ubiquitous organic compound whose main source is natural gas leakage and its mean diurnal curves are discussed above in Section 5.3.2. Night-time ethane concentrations are elevated over daytime mid-tropospheric values by accumulation within the nocturnal inversion layer and because of the generally poorer dispersion and lowest wind speed conditions that occur at night-time in urban areas. These diurnal variations are described in some detail in the Met. Office Box Model used within the system to produce the Department of the Environment, Transport and the Regions twice daily air pollution forecast. This model has been used to calculate the ethane concentrations in Central London for 0000-0600 hours on each day of 1995, assuming a constant natural gas leakage rate. Figure 5.21 compares 1042 model calculated and observed London UCL ethane concentrations during the April - September 1995 period. The slope of the correlation implies an ethane source strength of 3.95 t km^{-2} yr^{-1}. This compares well with the previous estimate of 3.56 t km^{-2} yr^{-1} based on a completely independent analysis of the Exhibition Road ethane data (Derwent *et al* 1995). The estimated ethane source strengths for each urban centre during April-September 1995, shown in Table 5.6, have been calculated from the respective night-time - mid-afternoon concentration differences in Table 5.4.

With the exception of ethane and propane, the majority of the low molecular weight C_2-C_8 hydrocarbons tend to behave as a consistent class of compounds across the range of sites in the UK hydrocarbons monitoring network. For example, they all exhibit similar shaped mean diurnal concentration curves when their weekday concentrations are averaged by hour-of-the-day, see Section 5.3.2. These weekday mean diurnal concentrations curves may be characterised by three main features:

- morning minima, usually between 0000 and 0600 hours,

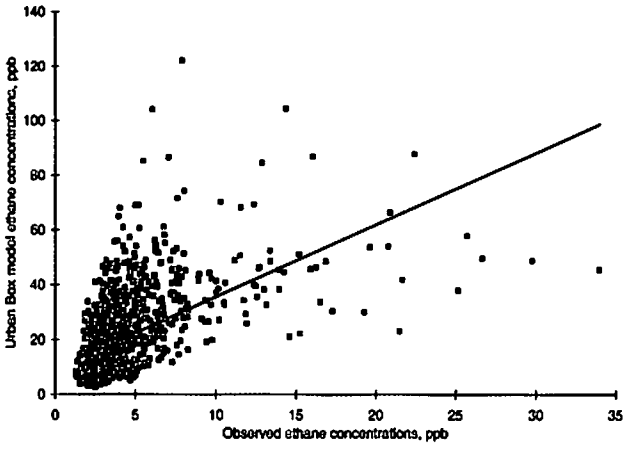

Figure 5.21 Comparison of the urban box model calculated ethane concentrations for central London for 0000 - 0600 hours each day between April - September 1995 and the observations for the London UCL site.

- morning maxima, usually between 0600 and 1100 hours,
- evening maxima, between 1500 and 2300 hours.

This characteristic weekday mean diurnal pattern is caused by the interplay between the diurnal cycles in emissions caused by human influences such as traffic flow and congestion and atmospheric dispersion factors, such as wind speed, boundary layer depth and turbulence. These two sets of cycles overlay to give ambient concentrations which peak during the morning and evening rush hours and reach a minimum during the night-time, off-peak hours. Such diurnal curves can be analysed to give emission rates for each of hydrocarbons for each of the sites.

We assume here that factors influencing atmospheric dispersion vary little across the population centres covered by the network during the April to September 1995 period. The concentration differences between the daily maxima and minima are assumed to be consequence of the difference in average emission densities between the sites. By normalising the diurnal patterns with a marker hydrocarbon, such as toluene,

Table 5.6 Estimates of ethane source strength for each urban centre from the night-time - mid-afternoon mean ethane concentrations difference during the period April-September 1995.

Site	Night-time – mid-afternoon concentration differences ppb	Ethane source strength, tonnes km^{-2} yr^{-1}
Edinburgh	1.77	3.59
London UCL (Bloomsbury)	1.95	3.95
London Eltham	2.40	4.86
Middlesbrough	3.01	6.10
Bristol	3.19	6.46
Southampton	3.36	6.81
Leeds	3.62	7.33
Birmingham	4.36	8.83
Cardiff	7.21	14.60

Note: no detectable natural gas leakage at Belfast hence no assessment has been made.

Table 5.7 Mean toluene concentrations observed at the network sites during the period April-Sept. 1995 and the estimates of mean toluene emission density derived from them.

Site	Mean toluene concentration, ppb	Mean toluene emission density, tonne km^{-2} yr^{-1}
Edinburgh	1.61	8.9
London UCL (Bloomsbury)	3.32	18.3
London Eltham	1.72	9.5
Middlesbrough	1.76	9.7
Bristol	2.13	11.7
Southampton	3.97	21.9
Leeds	1.76	9.7
Birmingham	2.03	11.2
Cardiff	1.79	9.9

Note: no detectable natural gas leakage at Belfast hence no assessment has been made.

the potential influence of gross differences between the different sites and hydrocarbons can be assessed.

The ratio of toluene to ethane during the period 0000 to 0600 hours from April to September 1995 at the London Eltham background site was found to be 0.2 ppb/ppb or 0.6 μg m^{-3}/μg m^{-3}. This allows an estimate to be made of the mean toluene source strength for London using the mean diurnal variation in motor vehicle traffic and the Met. Office Box Model as 9.5 t km^{-2} yr^{-1}. This compares well with the independent estimate of the toluene source strength for London of 4.3-7.5 t km^{-2} yr^{-1} based on the Exhibition Road, London data (Derwent *et al* 1995).

The estimated toluene source strengths for each urban centre during April-September 1995, calculated from the respective mean diurnal curves, are given in Table 5.7. Southampton and London UCL sites appear to have the highest toluene source strengths, presumably because they are roadside sites situated immediately close to busy roads. All the other sites exhibit toluene source strengths in the range 7.8-11.7 t km^{-2} yr^{-1}. The toluene source strengths of the urban centres using the urban background sites then rank in order of importance as:

Bristol > Birmingham > Cardiff > Leeds > Middlesbrough > London > Edinburgh > Belfast

Assuming that the coverage of the sites in Table 5.7 reflects the entire UK situation, then a total UK toluene emission can be estimated as 129 kt yr^{-1} compared with 147 kt yr^{-1} in Table 5.2.

Figure 5.22 presents the results of an analysis of the mean diurnal concentration curves at each site for each of the major C_2-C_8 hydrocarbons. Looking first at the aromatic hydrocarbons, benzene in particular, this figure presents for a particular site, the difference in mean benzene concentration between the morning and evening maxima and the early morning minima, expressed relative to the same quantities for toluene, over the April to September 1995 period. These ratios of benzene to toluene are then calculated for all the sites and displayed in Figure 5.22. The mean benzene to toluene ratio by concentration over all is found to be 0.51 ± 0.11. Figure 5.22 also shows the corresponding inventory benzene to toluene ratio of 0.39 expressed on a by volume basis. There therefore appears to be an underestimation of the benzene to toluene ratio in the current inventory which was also apparent from the Exhibition Road study, see Table 5.5.

Figure 5.22 shows the results of a similar analysis of all the mean diurnal curves for each hydrocarbon and site in turn, relative to toluene. Ethylbenzene appears to be largely accurately placed in the PORG inventory relative to toluene but the xylenes are significantly overestimated. For the olefins, the agreement between

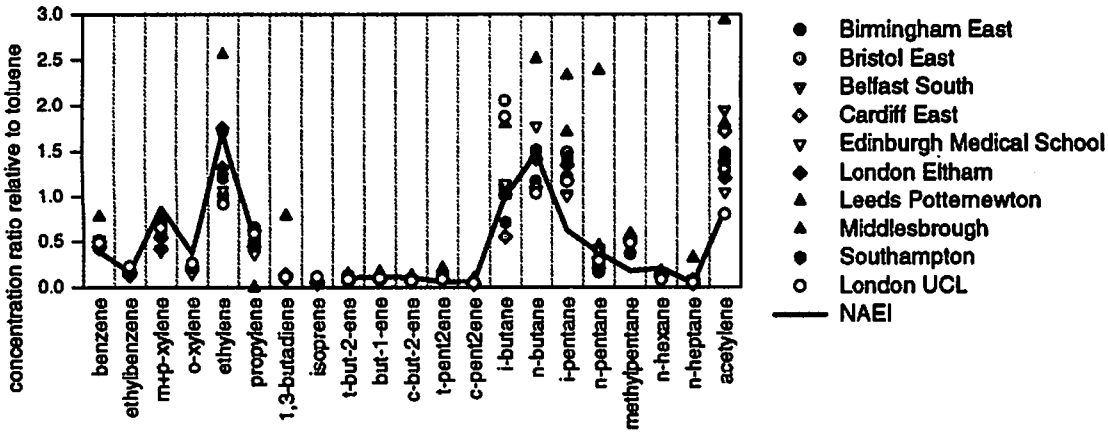

Figure 5.22 Differences in concentration between the morning and evening maxima and early morning minima expressed relative to those values for toluene at each HCN site and from the National Atmospheric Emissions Inventory (NAEI) during Apr-Sept, 1995.

the concentration ratios relative to toluene is rather good. The network data has allowed the determination of the likely UK emissions of the diolefins: 1,3-butadiene and isoprene from urban traffic which are not included in the current inventory.

For the alkanes, the inventory appears to underestimate their concentrations in most of the population centres of the hydrocarbons monitoring network. This underestimation is particularly pronounced for i-pentane and methylpentane and may be due to an underestimation of petrol evaporation emissions.

Attention is drawn in Figure 5.22 to the underestimation of the acetylene to toluene ratio in the inventory compared with the network measurements. Since acetylene is often taken as a marker for motor vehicle exhaust, this underestimation appears to be quite dramatic. A likely explanation of the discrepancy is problems with the analysis in the experimental set-up used for the determination of the vehicle exhaust emission factors.

Table 5.8 gathers together the total emissions of each hydrocarbon estimated using the hydrocarbon/toluene ratios observed in the network and the total toluene emissions of 129 kt per year determined above. The total emissions of all the C_2-C_8 hydrocarbons monitored in the network amounts to 1080 kt per year. When the non-transport, stationary sources are included, the total inventory amounts to 1452 kt per year. This total is somewhat higher compared with the PORG inventory total for these same species. It is therefore likely that the computer models used to describe ozone formation which are based on the current emission inventories significantly underestimate hydrocarbon emissions.

5.5 Role of Light Hydrocarbons in Regional Scale Ozone Formation

Having quantified the summertime mean hydrocarbons across the major urban and industrial-centres of the United Kingdom the next step is to identify their relative contributions to regional scale ozone formation. This can be done by examining the competition between the hydrocarbons for hydroxyl radicals in the urban background air as it moves out from the urban centres during daylight into the surrounding rural areas. Assuming that the dispersion and transport processes do not disturb the relative concentrations of the hydrocarbons, then the competition between the hydrocarbons for the hydroxyl radicals will determine their relative potentials for regional scale ozone formation through the reaction sequence:

$$OH + RH = R + H_2O$$
$$R + O_2 + M = RO_2 + M$$
$$RO_2 + NO = RO + NO_2$$

This type of analysis is a first approximation to provide a useful, practical mechanism with which to estimate ozone formation from a series of organic compounds. Chapter 2 deals in detail with the many factors which influence the formation of ozone in the atmosphere. It is assumed that there is an adequate supply of nitric oxide to ensure that all the peroxy radicals are quantitatively converted to carbonyl compounds and oxidise two molecules of NO to NO_2 through:

$$RO + O_2 = HO_2 + R'CR"O$$
$$HO_2 + NO = HO_2 + NO_2$$

Table 5.9 summarises the analysis of the observed ozone forming potential of the 87 hydrocarbons > C_2 complied from the available UK measurement studies.

Table 5.8 Concentration ratios relative to toluene and total UK emissions from transport and non-transport sources for each hydrocarbon.

	Concentration Ratio by Volume	Emissions ktonnes yr^{-1}	Non-transport Emissions ktonnes yr^{-1}
benzene	0.51	56	6
toluene	1	129	54
ethyl benzene	0.19	28	0.1
m+p-xylene	0.57	85	47
o-xylene	0.22	33	24
ethylene	1.98	78	9
propylene	0.52	31	5
1,3-butadiene	0.18	14	-
isoprene	0.07	7	-
tranbut-2-ene	0.10	8	3
but-1-ene	0.10	8	3
cis but-2-ene	0.08	6	3
transpent-2-ene	0.11	11	2
cis pent-2-ene	0.05	5	2
i-butane	1.23	100	-
n-butane	1.79	146	83
i-pentane	1.39	140	21
n-pentane	0.51	51	19
methylpentane	0.50	60	9
n-hexane	0.13	16	15
n-heptane	0.08	11	2
acetylene	1.56	57	0.5
Grand Total	-	**1080**	**371.6**

Table 5.9 Mean rural summertime concentrations, rate coefficients for reaction with OH radicals and estimated contributions to O_3 formation for each individual hydrocarbon measured in the UK.

Species	mean, ppb	OH + species k OH x 10^{12}	O_3 prod. ppb h^{-1}	Notes
i-butene	0.21	51.4	0.773	b
propylene	0.27	26.3	0.511	a
ethylene	0.67	8.52	0.411	a
isoprene	0.05	101	0.364	a
1,2,4-trimethylbenzene	0.15	32.5	0.352	c
m+p-xylene	0.21	19	0.287	a
1,3,5-trimethylbenzene	0.06	57.5	0.256	c
transbut-2-ene	0.05	64	0.23	a
toluene	0.46	5.96	0.197	a
transpent-2-ene	0.04	66.9	0.193	a
1,3-butadiene	0.04	66.6	0.192	a
cisbut-2-ene	0.04	56.4	0.162	a
i-pentane	0.52	3.9	0.146	a
o-xylene	0.14	13.7	0.138	a
but-1-ene	0.05	31.4	0.113	b
3-methyl-cis-pent-2-ene	0.02	86.7	0.112	c
n-butane	0.59	2.52	0.107	a
m-ethyltoluene	0.07	19.2	0.1	c
3-methyl-trans-pent-2-ene	0.02	86.7	0.097	c
2-methylpent-2-ene	0.02	89	0.097	c
cis-pent-2-ene	0.02	65.4	0.094	a
hexenes	0.02	47.9	0.082	c
acetylene	1.38	0.815	0.081	a
1,2,3-trimethylbenzene	0.03	32.7	0.079	c
3-methylcyclopentene	0.02	66	0.076	c
1,2,3,5-tetramethylbenzene	0.01	77	0.075	c
propane	0.74	1.15	0.061	a
2-methylpentane	0.15	5.6	0.06	a
decane	0.06	11.6	0.052	c
ethylbenzene	0.09	7.1	0.046	a
styrene	0.01	58	0.046	c
p-ethyltoluene	0.05	12.1	0.041	c
n-pentane	0.14	3.96	0.04	a
i-butane	0.23	2.33	0.039	a
1,2,4,5-tetramethylbenzene	0.01	65	0.037	c
ethane	1.87	0.257	0.035	a
o-ethyltoluene	0.04	12.3	0.034	c
14-dimethyl-2-ethylbenzene	0.01	32.5	0.033	c
12-dimethyl-4-ethylbenzene	0.01	32.5	0.032	c
2,3,4-trimethylpentane	0.05	8.7	0.03	c
3-methylpentane	0.07	5.7	0.03	a
a-pinene	0.01	53.7	0.027	c
2,2,4-trimethylpentane	0.1	3.6	0.027	c
13-dimethyl-4-ethylbenzene	0.01	32.5	0.026	c
methylcyclopentane	0.04	8.8	0.025	c
3-methylhexane	0.05	7.2	0.025	c
n-hexane	0.06	5.61	0.024	a
undecane	0.02	13.2	0.023	c
benzene	0.24	1.32	0.023	a
2-methylhexane	0.05	6.8	0.022	c
n-nonane	0.03	10.2	0.021	c
1-methyl-n-propylbenzene	0.01	21.4	0.019	c
2,3-dimethylhexane	0.03	8.6	0.018	c
methylcyclohexane	0.02	10.4	0.017	c
4-methylnonane	0.02	11.3	0.016	c
4-methyloctane	0.02	10	0.016	c
n-heptane	0.03	7.2	0.016	a
2-methylnonane	0.02	11	0.015	c
2-methyloctane	0.02	9.6	0.015	c
n-butylbenzene	0.03	6.4	0.015	c
n-octane	0.02	8.7	0.013	b
2,4-dimethylhexane	0.02	8.6	0.012	c
2-methylheptane	0.02	8.2	0.012	c
indane	0.02	9.2	0.012	c
2,3-dimethylpentane	0.02	7.2	0.012	c
dodecane	0.01	14.2	0.012	c
3-methylheptane	0.02	8.6	0.011	c
propylbenzene	0.02	6	0.011	c
1,3-diethylbenzene	0.01	21.4	0.011	c
dimethylheptanes	0.01	10	0.009	c

Table 5.9 continued

Species	mean, ppb	OH + species k OH x 10^{12}	O_3 prod. ppb h^{-1}	Notes
trans1,3-dimethylcyclopentane	0.01	10.6	0.009	c
propylcyclohexane	0.01	12.7	0.008	c
2,5-dimethylhexane	0.01	8.3	0.008	c
n-nonane	0.01	10.2	0.008	b
2,4-dimethylpentane	0.02	6.9	0.008	c
dimethyloctanes	0.01	11.4	0.008	c
cis-13-dimethylcyclopentane	0.01	10.6	0.007	c
3-methyloctane	0.01	10	0.007	c
2,3,3-trimethylpentane	0.02	4.4	0.007	c
cis-13-dimethylcyclohexane	0.01	12	0.006	c
cyclohexane	0.01	7.5	0.006	c
4-methylheptane	0.01	8.6	0.006	c
1,4-dimethylcyclohexane	0.01	12	0.006	c
dimethylcyclohexanes	0.01	12	0.005	c
1,1-dimethylcyclohexane	0.01	12	0.005	c
i-propylbenzene	0.01	6.5	0.003	c
2,2,5-trimethylhexane	0.01	6.1	0.003	c
Total			**6.557**	

a. 1st April to 31st August 1996 mean concentrations for Harwell site in the monitoring network
b. mean concentrations calculated relative to toluene from the hydrocarbon measurements reported for West Beckham and Great Dun Fell in the 3rd PORG report
c. mean concentrations calculated relative to toluene from the 21 day hydrocarbon monitoring study in Leeds (Bartle *et al* 1995)

The contribution from the C_2 - C_8 hydrocarbons has been based on the summertime observations from the hydrocarbon network monitoring site at Harwell, Oxfordshire using the April-September data for 1996. In addition, The Department of the Environment have commissioned the School of Chemistry at the University of Leeds to extend the range of hydrocarbons monitored at the local national hydrocarbon monitoring network site to the limits that are practical using simple gas chromatography in one intensive campaign. The study, carried out in the late summer of 1994 provides a unique and detailed analysis of the hydrocarbon speciation beyond C_6 at eight sites within the city. It provides some of the first measurements of long chain aromatics, alkenes and cycloalkanes in the UK and Europe. This dataset was ratioed to toluene and added to the hydrocarbon network site data for the Harwell site. Further data for the C_2 - C_8 compounds, again ratioed to toluene, were added from the rural measurements at West Beckham, Norfolk and Great Dun Fell, by the University of East Anglia.

The relative OH reactivities for all 87 of the $>C_2$ hydrocarbons are presented in rank order in Table 5.9. The values for the $>C_6$ hydrocarbons are significant compared to the corresponding values of the light hydrocarbons. It is clear that the aromatic hydrocarbons present in urban air make a significant contribution to photochemical ozone formation, although olefins take the first four positions in the top ten rankings.

The total ozone forming potentials of the 87 observed hydrocarbons amounts to 6.6 ppb per hour, a figure well able to account for the elevated ozone concentrations observed in the United Kingdom and in the rest of North West Europe. The top ten hydrocarbons: i-butene > propylene > ethylene > isoprene > 1,2,4-trimethyl benzene > toluene, account for 3.6 ppb per hour, about one half of the total production.

Olefins account for 53%, aromatics 28%, aliphatics 10% and the remainder cycloparaffins and other organic compounds. The 25 hydrocarbons routinely monitored at the rural automatic networks sites account for 55% of the ozone forming potential of the total 87 compounds. This site should therefore provide important information on the long term influence of policies on the ozone forming potential of the different hydrocarbons.

Two biogenic hydrocarbons appear in Table 5.9; isoprene and alpha-pinene, which account for 5.5% and 0.4% of the total ozone forming potential. On this basis, biogenic hydrocarbons are unlikely to account significantly for the elevated ozone concentrations observed in the United Kingdom.

5.6 Rural Measurements of Hydrocarbons

Measurements of numerous hydrocarbon species have been made at several rural sites in the UK (PORG 1993, Dollard *et al* 1995). Probably the site with the longest history of rural measurements in the UK is at Harwell in south east England. Measurements were first made in 1973 (Cox *et al* 1976) followed by further measurements from 1982 to 1983 (Sandalls and James 1984); measurements from 1985 to 1987 have been reported (Jones 1988) and more recently an automatic network site has been established at Harwell. Apart from the recent automatic measurements (Section 5.3.1) all measurements were based on grab samples followed by chromatographic determination using FID.

Figure 5.23 summarises data from the four periods; benzene and toluene were not reported for the two earlier studies. Figure 5.23a shows the data for ethane whose major emission source is leakage from natural gas supplies. The ethane concentrations reported for 1973 are high at about 15 ppb. This may have been due to a greater leakage of natural gas from the distribution network at this time or the influence of leakage from buildings in the vicinity of the sampling location (Sandalls and James 1984). It is worthy of note that the early samples for 1986 and 1987 (Jones 1988)

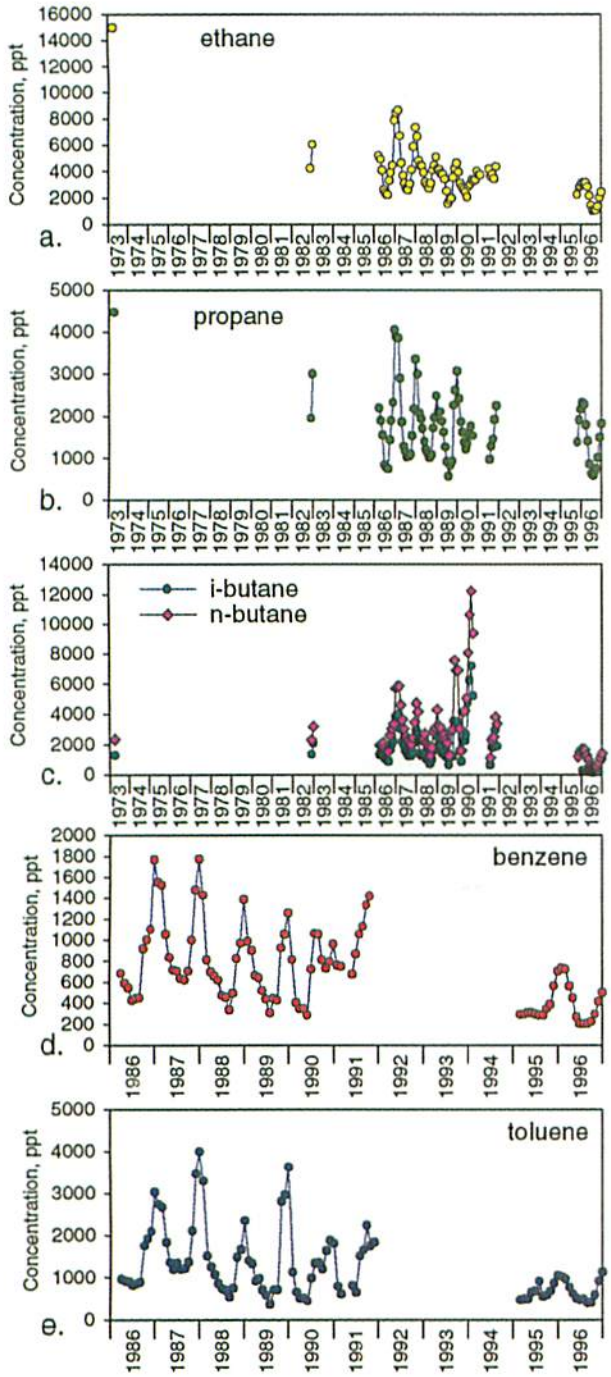

Figure 5.23 VOC measurements at Harwell.

were collected at approximately the same location as the early samples of Cox *et al* (1976). From 1988 onwards samples were collected at downwind locations away from the Harwell site. If the data for 1973 are valid it is apparent that there has been a substantial decline in rural ambient ethane over this period. Figure 5.23b illustrates the equivalent data for propane, again a substantial decline in concentrations for the period could be concluded. For both of these compounds the data from 1986 up to the present time show very strong seasonality.

Figure 5.23c summarises data for i and n-butane from 1973 through to the present. Concentrations are much more consistent between the periods and it is very interesting to note the indication that concentrations have increased slightly over the period. These two compounds originate primarily from evaporative losses; the apparent increase may reflect growth in the vehicle fleet over the period (and associated petrol distribution); this would be consistent with the data in Table 5.1 for evaporative emissions of petroleum.

Benzene data are illustrated in Figure 5.23d; these data are only available from 1986. There is a strong seasonality in the data with evidence of a downward trend in concentrations. Simple visual assessment suggests this is about -40% over the period 1986 to 1995; this is approximately the decline indicated for the Central London site implied by data presented by Field *et al* (1994). Toluene shows a similar seasonal behaviour to benzene.

Guicherit (1978) reports acetylene data collected during the 1970s at an industrially influenced site at Delft in the west of the Netherlands. The data for acetylene show an increasing trend of 4 to 5% per year consistent with expected vehicle emissions.

Roemer *et al* (1995) have examined C_2 to C_5 hydrocarbon measurements made over the period 1981-1991 at a rural site also in the west of the Netherlands (Moerdijk). The data show that at Moerdijk, concentrations of hydrocarbons have decreased substantially since the early 1980s. When averaged over all wind sectors there is an apparent downward trend which for acetylene is -3% per year during the 1980s (significant at 95% confidence interval). The decline supports estimates of a similar order decrease in hydrocarbon emissions from traffic in the Netherlands and Germany over this period. When samples only collected in background air were analysed by Roemer *et al* (1995), significant downward trends were noted for ethane, acetylene and propane.

The available measurement data from sites where studies have been carried out over several years suggest that in the UK concentrations of measured species of VOCs in the atmosphere have declined since the early 1970s. This apparent decline in ambient concentrations has occurred over a period when according to inventory statistics, total UK emissions of VOCs have increased slightly.

5.6.1 Measurements of Hydrocarbons at Mace Head

Air samples have been collected at Mace Head on the west coast of Ireland since 1993 and analysed by the University of East Anglia for C_2-C_8 hydrocarbons, sampling occurred approximately every two weeks and when the wind was ostensibly coming from the "clean westerly sector" (180° - 300° from north). The Mace Head site is an ideal location to sample air away from the influence of local sources.

Seasonal cycles

A composite seasonal cycle has been produced for each of the twenty-seven C_2-C_8 hydrocarbons that are routinely analysed at UEA. Figure 5.24 represents a selection of the alkanes that are measured. A clear annual cycle is evident with a pronounced summer minimum and winter maximum. In the case of man-made alkanes the reduction in concentration in the

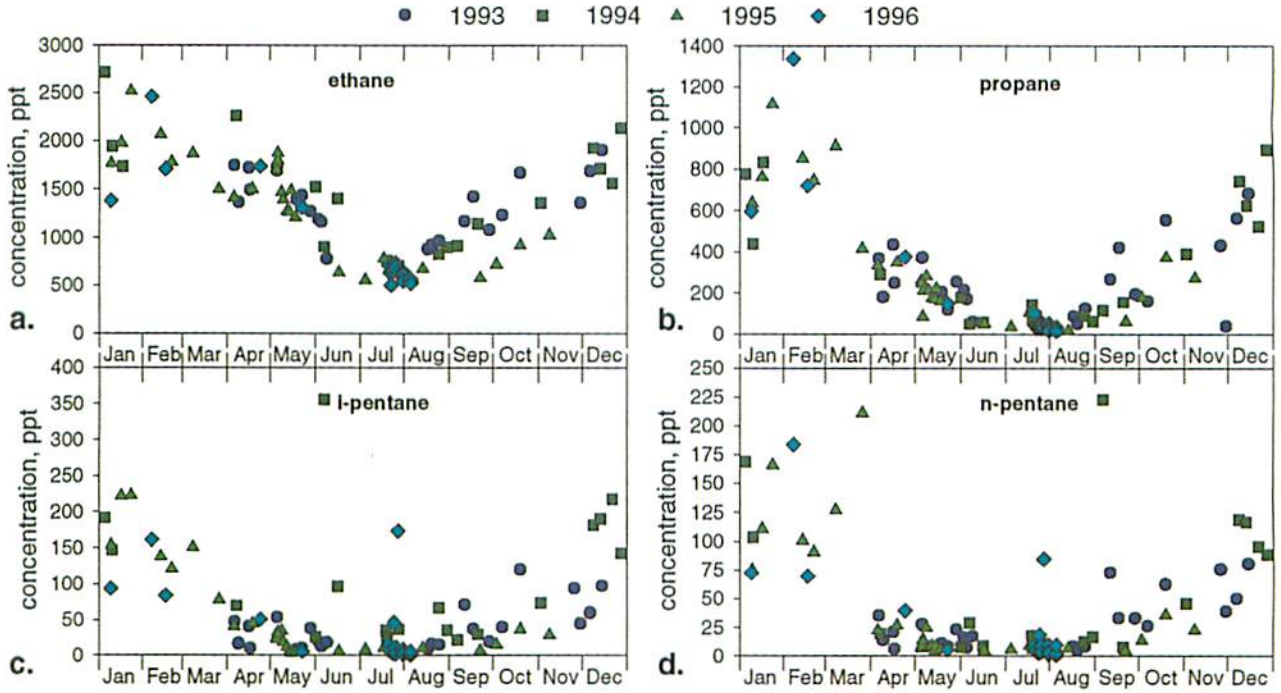

Figure 5.24 1993-1996 annual cycles in (a) ethane, (b) propane, (c) i-pentane and (d) n-pentane at Mace Head on the West coast of Ireland.

summer is predominantly due to enhanced depletion as a result of reaction with the hydroxyl radical.

The lifetimes of the straight-chain alkanes with respect to OH vary from 1.9 days for i-pentane to 29 days for ethane (Table 2.5). The summer minima in ethane and propane concentrations never fall below the minimum detection limit (Figure 5.24a and 5.24b). The chemical lifetime of ethane is greater than the transport time from the north American continent resulting in the non-zero background.

Lowest concentrations of ethane are approximately 600 ppt; these are below the minimum levels recorded at Harwell indicating that ambient concentrations of hydrocarbons in the UK are predominantly due to UK (and Irish) sources.

For propane, the background concentration measured at Mace Head in the summer is measurable although the chemical lifetime is less than the average transport time from the source region. Marine emissions may account for the non-zero measurements in the clean sector during the summertime.

Background concentrations of both i-pentane and n- pentane (Figure 5.24c and 5.24d) are very low during the summer at Mace Head (often below the minimum detectable limit (2 ppt)). This is because the sampled air mass has not had any new hydrocarbon input for several days but removal is still occurring due to oxidation by the OH radical.

For the shorter lived alkenes, shown in Figure 5.25 the picture is not quite so clear. Ethene and propene both have marine sources (Bonsang 1993, Boudries *et al* 1994, Ratte *et al* 1995) and the close proximity of the sampling station to the coast may be providing sufficient flux of these species for the observed concentrations to not be dominated by sink processes.

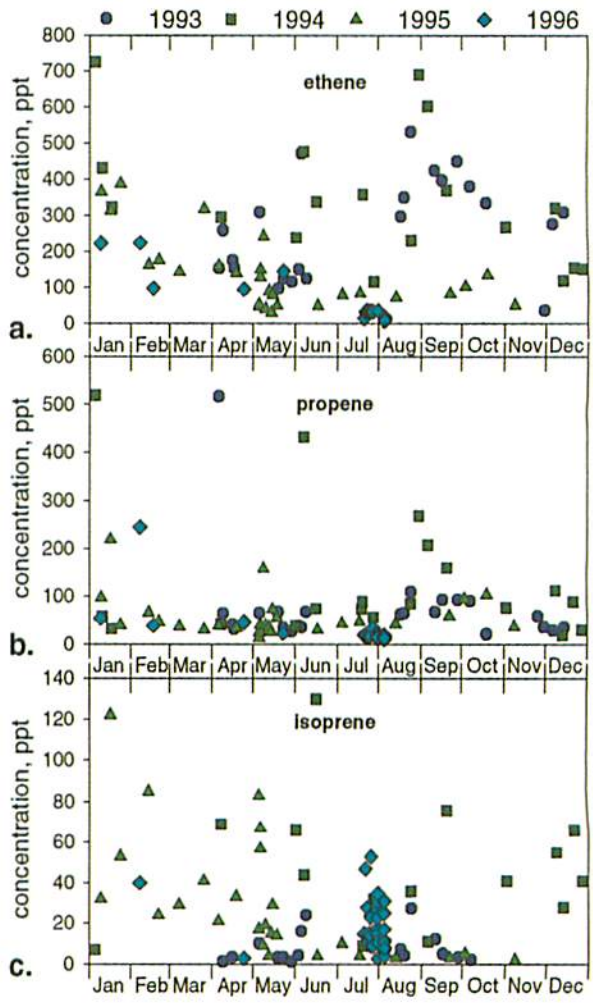

Figure 5.25 1993-1996 annual mean cycles in ethene, propene and isoprene at Mace Head.

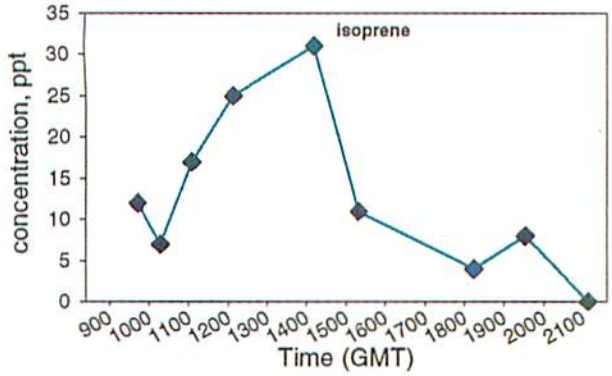

Figure 5.26 Mean diurnal cycle in isoprene at Mace Head.

Isoprene is generally thought of as a biogenic hydrocarbon, emitted by terrestrial plant-life. However, Burgess and Penkett (1993) found that air collected in the Dartford tunnel had measurable quantities of isoprene. These findings were supported by measurements in Ontario, Canada (Mclaren 1996) that motor vehicle exhaust provided a measurable source of isoprene.

Isoprene normally has a clear diurnal cycle with maximum concentrations appearing after solar noon due to biogenic emission fluxes being strongly influenced by temperature and net photosynthetically active radiation (PAR). However, in marine sector air a diurnal cycle was also observed, although at reduced concentrations compared with diurnal cycles of land-based origin. A flux of isoprene is apparent from Figure 5.26, although it is not possible to say from this whether the emission is from marine plant-life rather than direct emission from the sea.

All the different sources of isoprene (man-made, terrestrial biogenic and marine biogenic) are contributing to the measured concentrations (Figure 5.25c) which masks any clear seasonal pattern.

By contrast, dimethyl sulphide (DMS) has a distinct seasonal cycle with summer maximum and winter minimum as shown in Figure 5.27a.

These data are the longest set of land-based atmospheric DMS measurements made at one site in the northern hemisphere. The large concentrations of dimethyl sulphide observed in the summer months are likely to play a significant role in the sulphur and nitrogen cycles linked by the nitrate radical.

Acetylene is predominantly produced by motor vehicle exhausts, and benzene and toluene both have significant sources from motor vehicles, although toluene has additional solvent sources. The seasonal cycle of these three hydrocarbons are similar to the alkanes, as seen in Figures 5.27 b to d.

In all cases the year to year changes are fairly small but will probably be due to changes in particular meteorological conditions at the time of sampling.

5.7 Methane

Methane, of all of the hydrocarbons, is present in the atmosphere at the highest concentration. Global methane emissions amount to over 0.5 Gt yr^{-1} mainly

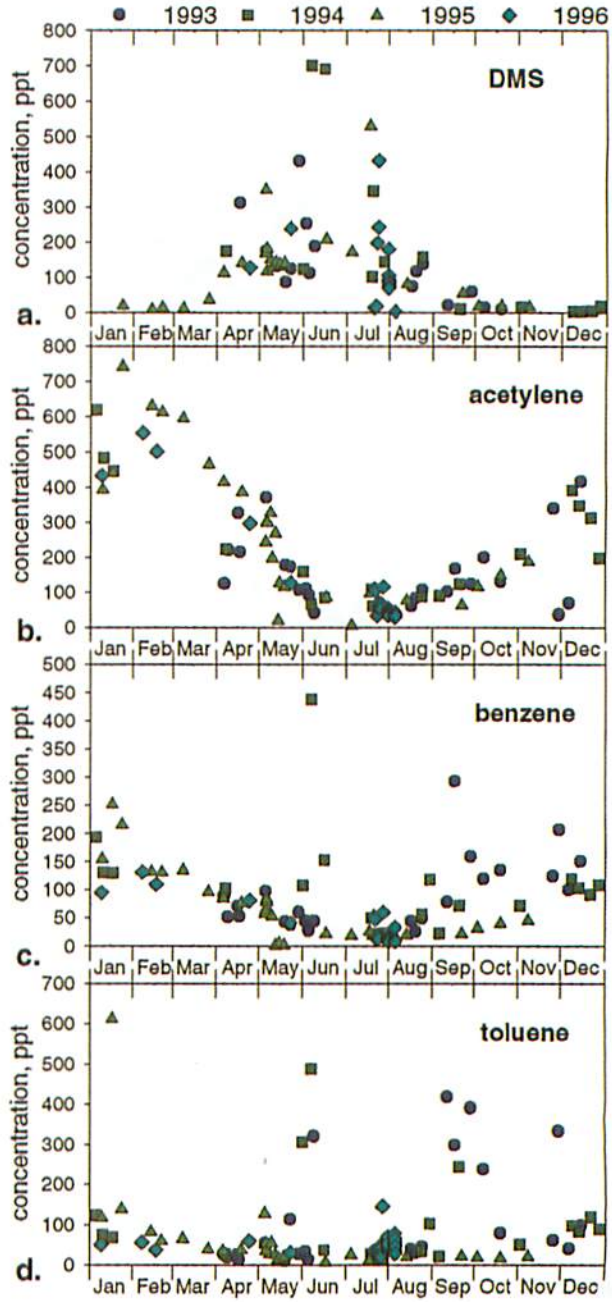

Figure 5.27 1993-1996 annual cycles in (a) DMS, (b) acetylene, (c) benzene and (d) toluene at Mace Head.

from animals and rice cultivation, buried domestic waste, wetlands and tundra, oil and gas exploration and biomass burning. The main atmospheric removal process for methane is oxidation by tropospheric hydroxyl (OH) radicals:

$$OH + CH_4 = CH_3 + H_2O$$

which is a key reaction in the fast photochemical balance of the troposphere and a source of much of the ozone found in the troposphere. Methane is the second most important radiatively-active gas after carbon dioxide and its life cycle has been significantly influenced by human activities since pre-industrial times.

Methane is routinely monitored in the British Isles at Mace Head, Ireland on the coast of the Atlantic Ocean,

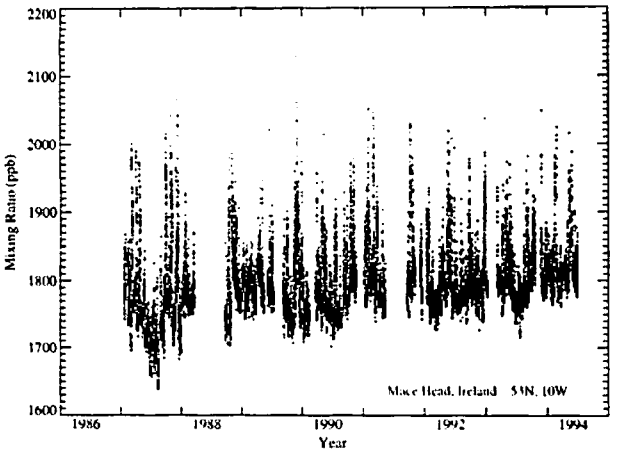

Figure 5.28 2 hourly average methane measurements at Mace Head for 1986 to 1994.

as part of the AGAGE programme. The available record since 1987 of 2-hourly methane measurements is illustrated in Figure 5.28. This shows the presence of a tropospheric baseline when clean Atlantic maritime air is advected to the Mace Head site. Superimposed on this baseline are irregular excursions representing major pollution events when dirty European air is advected to the site from the continent of Europe. Table 5.10 summarises the mean annual baseline methane concentrations observed at Mace Head which show a steady annual increase since 1987. Following the eruption of Mount Pinatubo in 1991, the rate of increase in the global baseline faltered somewhat during 1991-3 but the increase has now resumed.

By subtracting the methane baseline from the pollution peaks, estimates can be made of the methane concentrations in the pollution events due to European sources. Simple long range transport models can then be employed to work back from the methane peaks to estimate the magnitude of the methane emission source strengths that would be required to support the observations (see Table 5.10). The annual mean European source strengths for methane from all sources, have varied between 44 and 94 kg/head of population/yr and are somewhat lower than current emission inventory estimates of 72 kg/head of population/year within the CORINAIR emission inventory programme for the 29 countries of the European Union (European Environment Agency 1995).

In the United Kingdom, the NAEI estimates 1995 methane emissions as 4.17 Mt per year from human activities including agriculture, with landfill as by far the largest contributor. This estimate compares with the CORINAIR value of 3.39 Mt per year for 1990 where a significantly smaller contribution from landfill has been included. The Mace Head measurements point to a UK source strength of about 3.45 (2.4-5.2) Mt per year from all sources, both man-made and natural.

Methane through its role in the fast photochemical balance, makes a significant contribution to regional scale ozone formation. Computer modelling studies indicate that methane oxidation accounts for about 15-20% of the ozone formed photochemically over north west Europe (Hough and Derwent, 1987).

Table 5.10 Estimates of the global methane baseline concentrations and the European source strengths from the AGAGE methane monitoring data for Mace Head, Ireland over the period 1987-1995.

Year	Annual mean baseline methane concentration ppb	European methane source strength, Mtonnes yr^{-1} (kg/head.yr)
1987	1737	48 (94)
1988	1782	22 (44)
1989	1790	23 (45)
1990	1767	31 (62)
1991	1795	35 (69)
1992	1787	31 (61)
1993	1795	24 (47)
1994	1803	41 (81)
1995	1805	30 (60)

5.7.1 Methane from UK Wetlands

On a global scale wetlands are a major contributor to atmospheric methane, and the peatlands of the northern hemisphere are the single largest source. In the UK, extensive areas of peatland in the north and west, especially in Scotland, contribute natural emissions of CH_4 to the atmosphere. The rates of emission are very sensitive to temperature and water table, and spatial variability across total areas of peatland with a water table very close to the surface (within 10cm) are not well defined. The estimate of annual CH_4 emission for the UK wetlands of 120 kt as CH_4 (< 5% of UK emissions) reported by the Watt Committee (1994) must therefore be regarded as very uncertain.

5.8 Oxygenated Hydrocarbons

Researchers at the Norwegian Institute for Air Research (NILU) have been carrying out a programme of measurements of a range of oxygenated hydrocarbons across Europe. This is part of the activities of the European Monitoring and Evaluation Programme (EMEP). The UK Department of the Environment, Transport and the Regions have provided funding to NETCEN to facilitate measurements in the UK at Harwell in the south of England.

The EMEP measurement programme has been in operation for some time and the methodology has been developed and improved over this period. The compounds measured are given in Table 5.11. The compounds are sampled using cartridges containing 2,4 dinitrophenylhydrazine-coated silica packed into polyethylene tubes. The air samples are collected downstream of an ozone scrubber. After exposure the cartridges are eluted with acetonitrile and analysed with reversed phase HPLC using UV detection.

Table 5.12 summarises the monthly mean concentrations of the simple aliphatic aldehydes from monitoring at the rural Harwell site during 1994. Monthly mean formaldehyde concentrations cover the range 0.8-3.0 ppb and show a clear summer maximum. Acetaldehyde concentrations follow those of formaldehyde quite closely, at about the same concentration level on by volume basis, and again show a summer maximum. Higher homologues, up to

Table 5.11 Carbonyl Compounds Measured on EMEP Programme at Harwell.

formaldehyde	-	methanal
acetaldehyde	-	ethanal
propionaldehyde	-	propanal
butyraldehyde	-	butanal + 2-methylpropanal (i-butanal)
valeraldehyde	-	pentanal
caproaldehyde	-	hexanal
acetone	-	propanone
methylethylketone	-	butanone
acrolein	-	propenal
methylvinylketone	-	3-buten-2-one
methacrolein	-	2-methylpropenal
benzaldehyde	-	benzenecarbonal/phenylcarbaldehyde
glyoxal	-	ethandial
methylglyoxal	-	2-oxopropanal

the C_6-aldehyde, are present at the rural Harwell site, but with decreasing concentration. Aldehydes, as a family, appear to have a baseline concentration upon which pollution events are superimposed. Since these pollution events can occur both in the summer and the winter, it is assumed that there must be both significant direct emission of the aldehydes and photochemical production occurring to different extents during different times of the year.

The first two members of the homologous series of ketones have been monitored regularly at the rural Harwell site (Solberg *et al* 1995). The monthly mean concentrations of acetone and methylethylketone are presented in Table 5.13. The mean concentrations of acetone are easily the highest of all the oxygenated compounds detected at this site with typical monthly mean concentrations in the range 2-10 ppb. At this level, it is significantly higher in concentration than many of the low molecular weight hydrocarbons. Methylethylketone levels are about a factor of three below those of acetone.

Similar concentration distributions between formaldehyde, acetaldehyde and acetone have been reported for the Danish TOR site, 35 km west of Copenhagen, Denmark (Christensen *et al* 1994) and for the TOR Station on the summit of the Wank mountain, Germany (Slemr *et al* 1993).

Bifunctional carbonyl compounds are found in the atmosphere from the photochemical oxidation of hydrocarbons and some have been routinely detected at Harwell. Table 5.14 presents the mean monthly bifunctional carbonyl concentrations at Harwell prepared from the monitoring data of Solberg *et al* (1995).

The bifunctional carbonyl compounds appear to be dominated by the presence of glyoxal and methyl glyoxal. Their main source is the photochemical oxidation of the aromatic hydrocarbons emitted by human activities. Their detection gives strong support to the photochemical modelling studies which have indicated the importance of the photo-oxidation of aromatic hydrocarbons as an ozone source in north west Europe.

Table 5.13 Monthly mean atmospheric concentrations in ppb of the simple aliphatic ketones measured at Harwell, Oxfordshire as part of the UN ECE EMEP programme during 1994 (Solberg *et al* 1995). Concentrations in ppb.

Month of 1994	Acetone, propanone	methylethylketone, butanone
Jan	2.78	0.66
Feb	4.04	2.91
Mar	2.42	0.60
Jul	9.88	2.13
Aug	5.75	1.22
Sep	4.97	1.35
Oct	6.94	2.03
Nov	4.37	1.24

The unsaturated carbonyl compounds, methylvinylketone and methacrolein are barely detectable at the Harwell site, despite a relatively low minimum detectable sensitivity (Solberg *et al* 1995). These two unsaturated carbonyl compounds are the main breakdown products following the photo-oxidation of isoprene and have been used to infer the relative importance of the photochemical oxidation of biogenic vs man-made hydrocarbons as a source of ozone. The monthly mean concentrations of these two unsaturated carbonyl compounds peak during the summertime in July when isoprene photo-oxidation is expected to be most important. However, in August these compounds could not be detected and it is difficult to understand why they were so different from the July levels.

The concentrations of the unsaturated carbonyl compounds are sensitive indicators of the OH radical initiated photo-oxidation of isoprene. The observed mean concentrations of methylvinylketone and methacrolein in a rural forested site in western Alabama, USA were 740 and 480 ppt, respectively, (Montzka *et al* 1995). The observed concentration ratio of methylvinylketone and methacrolein in western Alabama agree well

Table 5.12 Monthly mean atmospheric concentrations in ppb of the simple aliphatic aldehydes measured at Harwell, Oxfordshire as part of the UN ECE EMEP programme during 1994 (Solberg *et al* 1995).

Month in 1994	methanal, formaldehyde HCHO	ethanal, acetaldehyde, CH_3CHO	propanal, propionaldehyde, CH_3CH_2CHO	butanal+ i-butanal, butyraldehyde	pentanal, valeraldehyde	hexanal, calproaldehyde
January	0.87	1.05	0.33	0.33	0.18	0.13
February	1.22	1.94	0.48	0.25	nd	0.50
March	0.76	1.01	0.30	0.17	0.11	0.35
July	3.02	3.14	0.67	0.44	0.46	0.44
August	2.86	2.35	0.53	0.78	nd	0.27
September	1.84	1.57	0.37	0.26	0.41	0.14
October	2.84	3.57	1.12	1.05	0.50	0.38
November	1.42	1.69	0.48	0.32	0.38	0.20

Notes: nd - no detectable

Table 5.14 Monthly mean atmospheric concentrations in ppb of the simple bifunctional carbonyl compounds measured at Harwell, Oxfordshire as part of the UN ECE EMEP programme during 1994 (Solberg *et al.* 1995).

Month of the year	Propenal, acrolein	methylvinyl-ketone 3-buten-2-one	2-methylacrolein 2-methylpropenal	benzaldehyde, phenylcarbaldehyde	glyxol ethandial	methylglyoxal 2-oxo-propanal
January	0.14	nd	nd	nd	0.12	0.18
February	nd	nd	nd	0.46	0.27	0.50
March	0.02	0.09	nd	0.14	0.13	0.35
July	0.12	0.55	0.23	0.6	0.06	0.44
August	nd	nd	nd	nd	nd	0.27
September	0.06	nd	nd	nd	0.12	0.14
October	0.13	nd	0.04	nd	0.21	0.38
November	0.07	nd	nd	nd	0.10	0.20

Notes: nd - no detectable

Table 5.15 Measured deposition velocities (in μm s^{-1}) and the OH rate coefficients for selected hydrocarbons.

	1,3-butadiene	ethene	n-hexane	benzene	acetylene
Spinach	78	74	43	48	2
Grass	82	150	49	56	65
Soil	63	27	22	27	16
Sea Water	1.5	1.6	3	1.4	1.6
Rate Coefficient $k_{OH} \times 10^{12}$	66.6	8.52	5.61	1.23	0.90

with the value of the ratio expected from isoprene photo-oxidation. The values reported in July 1994 for the rural Harwell location are in a similar ratio, but at a somewhat lower concentration compared with the USA measurements.

The agreement between the relative concentration ratios observed at Harwell and western Alabama is encouraging and points to the occurrence of isoprene photo-oxidation in rural southern England. Nevertheless, the absolute concentrations are lower compared with those reported in the USA (Montzka *et al* 1995). If account is taken of the non-detectable levels found during August and September, this would indicate a reduced importance of biogenic sources in rural southern England.

5.9 Estimates of the Dry Deposition of Selected Hydrocarbons

The rate at which a pollutant deposits to the earth's surface is an important factor in understanding its behaviour and impact on the environment. There are no reported data on the rate of removal of hydrocarbons to surfaces. From an understanding of the physical mechanisms involved in transport and the main chemical properties of hydrocarbons it has been assumed that removal rates are low and as such are unlikely to influence the atmospheric lifetime of a species.

A series of chamber experiments have been carried out by NETCEN to investigate the process of hydrocarbon deposition (Dore pers. comm., 1996). The compounds studied were: benzene, 1,3-butadiene, ethene, acetylene and hexane to give a range of molecular masses and molecule type.

Deposition was assessed for several surfaces:- grass, spinach, bare soil and water. This gave a variation in plant canopy type, leaf area index (LAI), and enabled estimates of the relative importance of the soil and canopy removal to be made.

Table 5.15 summarises the data and for comparison gives the rate coefficient for reaction with OH as a measure of the general reactivity of the molecule. There are differences between the hydrocarbon species and a good correlation with the OH rate coefficient, but overall the dry deposition rate is very small, confirming the conclusion that surface removal of these compounds is not significant.

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6. EMISSIONS AND CONCENTRATIONS OF OXIDISED NITROGEN COMPOUNDS

- Emissions of NO_x in the UK peaked in 1990 at 822 kt NO_x-N and in 1994 were 675 kt.
- Most of UK NO_x emissions (83%) are exported from the country, as NO_2, by the wind. The deposition of oxidized nitrogen as dry deposited NO_2 and wet deposited NO_3^- of 142 kt N represents 17% of emissions.
- In some large conurbations NO_x concentrations have declined over the last 5 years in line with national emissions (~ -20%). However, NO_2 concentrations in such areas have changed little as they are governed by the supply of O_3 for oxidation of the primary emissions of NO.
- Close to major conurbations there is evidence that rural NO_2 concentrations have increased since the 1980s, and throughout the UK, NO_2 concentrations are substantially larger than SO_2. However, most rural areas show a small decline in NO_2 concentrations over the period 1987 to 1995.
- In urban areas NO_x concentrations exceed the European Commission guide values and NO_2 concentrations exceed the European Union limit values. These exceedances are expected to decline as urban NO_x emissions decline over the next 5 years.
- Epidemiological studies have shown that day to day variations in concentrations of NO_2 are associated with adverse health effects. These studies include both time-series studies of daily hospital admissions and geographical studies comparing lung function in different areas. Although these effects may not be as marked as those associated with ozone and particles they are significant and, from the health standpoint, NO_2 remains an important air pollutant.
- The toxicity of ambient air pollution mixtures characterised by raised concentrations of NO_2 seems greater than that of NO_2 itself at similar concentrations. This apparent anomaly could be explained by associations between NO_2 and other pollutants.
- Studies of the effects of exposure to NO_2 indoors have shown an association between the presence of gas cookers and respiratory symptoms in asthmatic and non-asthmatic subjects, mostly children. More work is needed to identify the causative agent though a number of workers have suggested that NO_2 may be an important factor.
- In a study of an episode of pollution in London in 1991, characterised by high levels of NO_2 and particles, adverse health effects were detected but it was not possible to distinguish between the possible effects of particles and NO_2.
- Because of new knowledge of the important phytotoxic effects of nitric oxide (NO) the present critical level for impacts of nitrogen oxides on vegetation is a combined value for NO plus NO_2 (termed NO_X). The critical level is 30 µg m^{-3} (NO_2 equiv.) as an annual mean and applies to NO_X for all categories of vegetation.
- Estimates of NO_X distribution have been derived, using urban and rural conversion factors, from mapped values of NO_2. The critical level for effects of NO_X on vegetation is exceeded over 29% of the UK land area, particularly in rural central and southern England, and in and around major urban areas. In areas where the critical level is exceeded there may be adverse direct effects of NO_X on vegetation although the nature of the effects is uncertain. Semi-natural vegetation is potentially the most sensitive to NO_X exposure because it is often limited by the supply of nutrient nitrogen.

6.1 INTRODUCTION

The major man-made atmospheric oxides of nitrogen are nitric oxide, NO, and nitrogen dioxide, NO_2. The sum of these compounds is known as NO_x and explicitly excludes the other abundant atmospheric oxide of nitrogen, nitrous oxide, N_2O, which, although important as a greenhouse gas, does not participate actively in atmospheric chemical processes in the lower atmosphere and is not of importance in relation to ground-level ozone. On the contrary, however, nitric oxide and nitrogen dioxide are chemically involved in the formation and removal of ground-level ozone (see Chapter 2) and no discussion of the occurrence and chemistry of ozone in the lower atmosphere is complete without a consideration of NO_x. This chapter reviews the emissions and airborne concentrations of NO and NO_2. Additionally, it considers some other forms of oxidised nitrogen such as nitric acid, HNO_3 and nitrous acid, HONO, which are derived from atmospheric reactions of nitrogen dioxide. Other components of total oxidised nitrogen, collectively known as NO_y, such as PAN are dealt with in Chapter 4.

The importance of NO_x lies in a number of areas. As already mentioned, NO_2 is an important contributor to ozone formation in the lower atmosphere, whilst nitric oxide reacts with ozone temporarily removing it. Nitrogen dioxide is also important as a toxic gas in its own right, having the potential for adverse health effects on humans and causing damage to growing plants. When deposited to the earth's surface, oxidised nitrogen leads to nitrate enrichment of soils and surface waters which can in turn lead to a reduction in species diversity and eutrophication of water bodies. Nitric and nitrous acids formed in the atmosphere from NO_2 are important contributors to nitrogen deposition, and additionally, as described in the atmospheric chemistry chapter, nitrous acid may be photolysed in the atmosphere con-

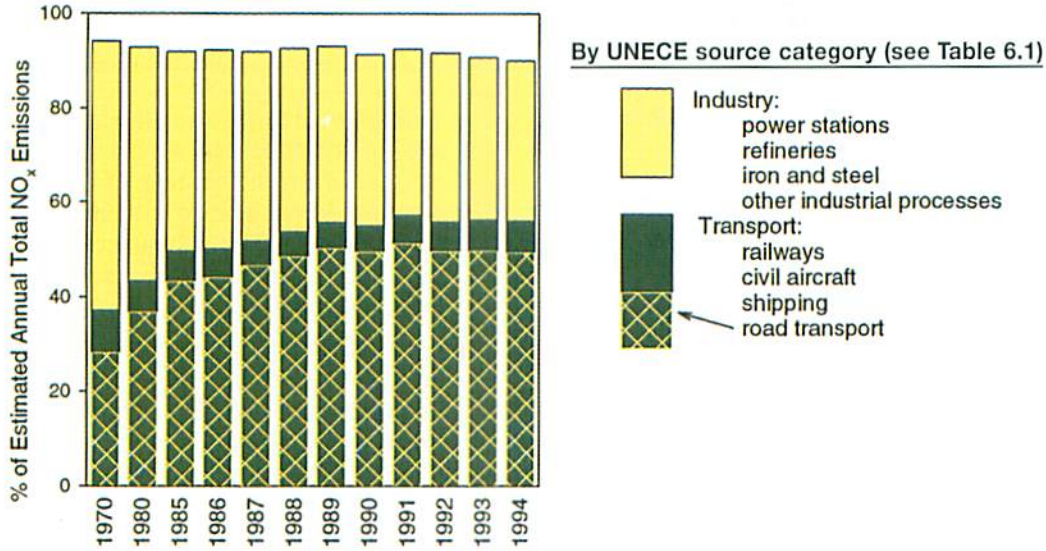

Figure 6.1 Estimated NO_x emissions from industry and transport in the UK by UNECE source category.

tributing an important source of the hydroxyl free radical.

This chapter reviews the sources and airborne concentrations of NO_x. Considerable further atmospheric concentration data has been collected since the Third Report, an it is now possible to comment further on trends in atmospheric concentrations for these species. Additionally, the understanding of nitric and nitrous acids in the atmosphere has been extended and brief reviews of the behaviour of these compounds are included.

6.2 UK Sources and Emissions of NO_x

The latest UK inventory of NO_x emissions (Dept. of Environment, 1995) by source category, end-user and type of fuel appears in Table 6.1. Two types of source dominate the emissions, see Figure 6.1. These are road traffic, contributing 53% of emissions in 1994 (by end user) and power stations which contributed 24%. In urban areas motor vehicles provide more than 70% of the ambient ground-level NO_x and about 50-70% in heavily populated rural areas of the UK. The power stations are high level sources which disperse their contribution very widely and contribute small concentrations over very large geographic areas. The inventories indicate that emissions of NO_x from power stations have been diminishing from a peak in 1987 and are now considerably reduced mainly as a result of introduction of low-NO_x burners and flue gas cleaning systems. Emissions from road traffic peaked in 1989 and were relatively steady from 1988 to 1992. Between 1992 and 1994 a significant decline occurred reflecting the European Community regulations requiring the fitting of three-way catalytic converters to all new cars from January 1993. Figure 6.1 shows the relative contributions from industry and transport (as a whole) over the period.

A spatially disaggregated emission inventory, shown in Figure 6.2, highlights the fact that the largest emissions of nitrogen oxides occur in urban areas together with high emissions in some less heavily populated areas where power stations are sited.

6.2.1 Soils as a Source of NO_x

Microbial processes in soils generate NO directly through both nitrification and denitrification.The emission may be regarded as leakage of a volatile intermediate during the chemical reduction of NO_3^- to N_2 (denitrification) and during the oxidation of NH_4^+ to NO_3^- (nitrification). Rates of NO production in aerobic soils range from 1% to 4% of the NH_4^+ oxidized. Rates of NO production during denitrification have been estimated to produce twice as much NO as nitrification but the net release of NO from soil is greatly influenced by diffusivity and in water-logged anaerobic soils, much of the NO produced is consumed by denitrifiers before release to the atmosphere.

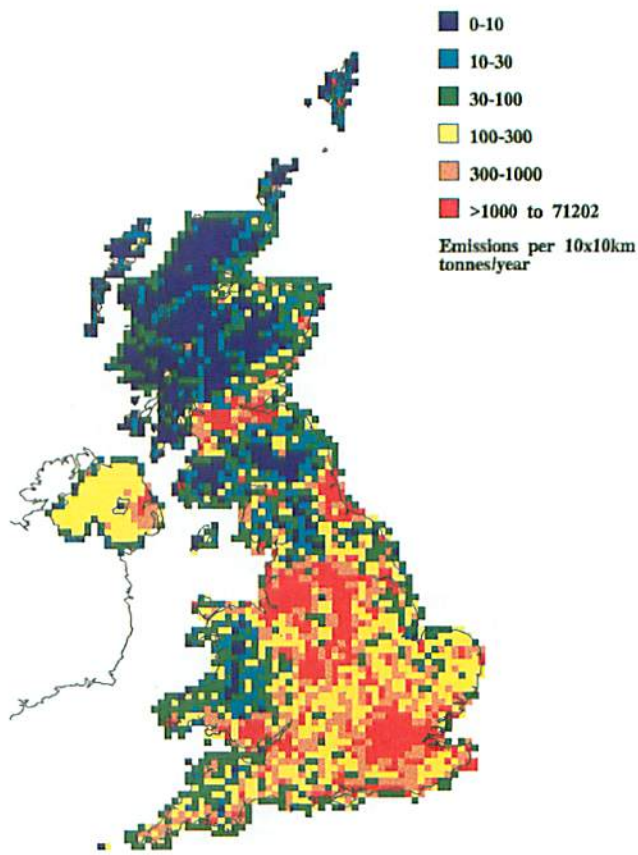

Figure 6.2 UK emissions of nitrogen oxides, spatially disaggregated from the 1993 emissions inventory (provided by AEAT, NETCEN).

On balance, nitrification is regarded as the major source of emitted NO for UK soils (Skiba *et al*, 1992). Typical rates of emission range from 1 to 50 ng NO-N m^{-2} s^{-1}, with the major variables regulating rates of emission from soil being NO_3^-, soil temperature and the water filled pore space. Using land use data and published emissions of NO for a range of soils Skiba *et al* (1992) estimated UK soil emission to be equivalent to approximately 65 kt NO_2 annually. This source is small and represents only *ca* 9% of anthropogenic emissions (700 kt), but is also rather uncertain and may be as large as 130 kt NO_2 annually.

6.3 Inter-Conversion of NO and NO_2

Emissions of NO_x from combustion sources such as road traffic and power stations are mainly in the form of NO. Since the emissions regulations refer to total NO_x, few measurements of the partition between NO and

Table 6.1 Estimated emissions[1] of nitrogen oxides (NO_x)[2] by UNECE source category end user[3] and type of fuel: 1970-1994.

United Kingdom													Thousand Tonnes
	1970	1980	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	% of total in 1994
(a) By UNECE source category													
Power stations	809r	846r	747r	777r	796	776r	773r	781r	680r	669r	579r	526	24
Domestic	62r	65r	68r	70r	70r	66r	63r	64r	71r	69r	72r	69	3
Commercial/public service	45r	42r	41r	42r	37r	39r	36r	35r	37r	36r	35r	34	2
Refineries	40r	45r	38r	40r	38r	39r	40r	4r	42r	43r	45r	45	2
Iron and steel	124r	42r	46r	42r	47r	51r	49r	47r	46r	44r	45r	48	2
Other industrial combustion	293r	195r	146r	149r	142r	150r	141r	137r	139r	134r	129r	128	6
Non-combustion processes	10	11	13	13	13	9	9	8r	7r	7r	6r	5	-
Extraction and dist. of fossil fuels[4]	8	44	66	68	73	76	78	82	85	88	103r	109	4
Road transport	636r	853r	1,019r	1,075r	1,192r	1,281r	1,369r	1,339r	1,332r	1,247r	1,163r	1,095	49
Railways	37r	28r	25r	25r	24r	24r	22r	21r	22r	22r	21r	21	1
Civil aircraft[5]	5	10	11	11	12	13	14	14	14	14	15	15	1
Shipping[6]	163	121	116	116	99	105	120	117	123	124	119	115	5
Waste treatment and disposal	12	12	12	12	12	12	12	12	12	12	4	4	-
Agriculture	7r	4r	4r	4r	3r	3r	3r	3r	3r	3r	3r	3	-
(b) By end user													
Domestic	412r	406r	358r	363r	363r	343r	334r	337r	314r	312r	281r	259	12
Commercial/public service	87r	101r	95r	93r	90r	88r	83r	84r	84r	91r	73r	70	3
Industry	710r	545r	454r	477r	484r	494r	483r	480r	435r	416r	383r	368	17
Agriculture	23r	21r	18r	18r	17r	17r	16r	16	14r	14r	13r	12	1
Road transport	649r	886r	1,067r	1,126r	1,245r	1,336r	1,427r	1,401r	1,383r	1,310r	1,231r	1,169	53
Other transport	222r	180r	177r	170r	160r	168r	183r	187r	189r	193r	191r	187	8
Miscellaneous	118r	141r	146r	153r	155r	158r	163r	159r	139r	136r	125r	114	5
Exports	7	14	13r	13	17	19r	18	18r	23r	22r	30r	28	1
Other emissions	23	24	25	25	25	22	21	21	20r	19r	10r	9	-
(c) By type of fuel													
Coal	938r	869r	740r	815r	847r	820r	820r	813r	720r	698r	584r	536	24
Solid smokeless fuel	82	6r	6	5	5	4r	4	4	4	4	5	5	-
Petroleum:													
Motor spirit	286r	443r	590r	635r	702r	761r	825r	828r	828r	787r	718r	653	29
DERV	350	411	429	441	490	520	544	511r	494r	460r	445r	442	20
Gas oil	130r	148r	145r	135r	124r	129r	141r	140r	142r	142r	134r	127	6
Fuel oil	428r	219r	188r	149	122	139	123r	128r	124	130r	139	124	6
Burning oil	9r	5	5r	5r	5r	5r	5r	5r	6r	6r	6	7	-
Other petroleum	27r	38r	39r	42r	43r	44r	46r	46r	47r	47r	49r	50	2
Other gas	42r	110r	118r	116r	121r	115r	113r	116r	122r	120r	132r	142	6
Other emissions	32r	69r	92r	94r	99r	105r	108r	112r	116r	120r	126r	133	6
TOTAL	**2,251r**	**2,318r**	**2,352r**	**2,437r**	**2,558r**	**2,643r**	**2,728r**	**2,702r**	**2,602r**	**2,513r**	**2,338r**	**2,218**	**100**
(d) Emissions from large combustion plants													
Large plants[7]	1,092r	1,032r	902r	933r	949r	935r	926	930r	749	742	636	676	
Index (1980 = 100)	106	100	87	90	92	91r	90r	90r	73r	72r	62r	55	
(e) Emissions (tonnes)/gdp (£million)[8]													
	6.6	5.7	5.2	5.1	5.1	5.0	5.0	5.0	4.9	4.7	4.3	3.9	

1 Most of the figures in this table are based on a single nitrogen for each fuel which are held constant over time.
2 Expressed as nitrogen dioxide equivalent.
3 Figures for end users include emissions from power stations which have been allocated, on an approximate basis, to the various sectors according to their use of electricity generated. They also include allocations of emissions from other secondary fuel producers.
4 Includes emissions from gas flaring and producers own use of gas on offshore installations. Also includes a small contribution from fuel oil use on offshore installations which is also included under shipping. This contribution is expected to be no more than 5 thousand tonnes in 1991.
5 Includes only those emissions associated with ground movement and take off and landing cycles up to 1 km from the airport.
6 Includes emissions from fishing, coastal shipping, oil exploration and production and includes fuel oil use on offshore installations. Includes only those emissions from marine bunker fuels from shipping within coastal waters (< 12 miles).
7 Power stations, refineries and a proportion (57 per cent up to 1990) of iron and steel, other industrial combustion, non-combustion processes and waste treatment and disposal. Figures for 1991 to 1994 are totals of those now published by HMIP on emissions from individual LCPs. The figures from 1991 onwards indicate that earlier LCP emission estimates may have been over-estimated.
8 GDP measured at 1990 prices.

NO_2 in exhaust gases have been made. In order to quantify the ratio of NO_2 to NO in road traffic emissions, measurements of the two compounds were made in a Birmingham road tunnel (Harrison and Shi, 1996). The results, shown in Figure 6.3, after correction for inter-conversion by reaction with background atmospheric ozone indicate that the percentage of NO_2 in NO_x emissions from traffic is generally low, about 5%, and even in slow moving traffic, increases to only about 7-8%. Emissions into the open atmosphere are followed by mixing with ambient air, and oxidation of NO to NO_2 occurs on a timescale of a few seconds by reaction with ambient ozone.

$$NO + O_3 \rightarrow NO_2 + O_2$$

This process is, however, limited by the availability of ozone in background air and this restricts the production of NO_2 under most circumstances. In sunlight, some reversal of this process may occur as a result of photolysis of NO_2 as described in Chapter 2. However, in urban air the dominant process is production of NO_2 with loss of ozone, and as noted elsewhere in this report, urban ozone concentrations tend to be lower than those in surrounding rural areas because of this chemical reaction.

At very high concentrations of NO_x other mechanisms become important in the conversion of NO to NO_2. The simplest of these is the third order reaction of NO with molecular oxygen

$$2NO + O_2 \rightarrow 2NO_2$$

The rate of this reaction depends on the square of the nitric oxide concentration, and hence it is very slow at low concentrations, but accelerates rapidly as the NO concentration increases. In practice the rate becomes significant in the atmosphere when the NO concentration approaches one part per million, as in pollution episodes. Under these conditions there is an acceleration in production of NO_2, but an analysis of the data from the December 1991 London air pollution episode has indicated that NO_2 production is still more rapid than can be accounted for by this reaction (Bower *et al* 1994) . Thus, other mechanisms must also be invoked and these are currently still the subject of research.

The relationship between hourly average NO_2 and NO_x, illustrated in Figure 6.4 with data from Exhibition Road, London (QUARG 1993), shows three distinct regimes. The first is for NO_x concentrations below about 30 ppb where the system is *NO_x-limited* as ozone is in excess. Here, NO_2 concentrations increase rapidly with increasing NO_x because of the rapid oxidation with ozone. As NO_x concentrations increase further, there is a relatively flat section from about 100-500 ppb NO_x. In this regime mean NO_2 increases by only about 30 ppb for a 400 ppb increase in NO_x. This can be accounted for in part through primary NO_2 emissions, and at the upper end of this range there will also be a small contribution from the NO_2 reaction with molecular oxygen. Above 500 ppb NO_x the curve begins to rise more sharply and it is here that the oxidation of NO by molecular oxygen and other species becomes more important.

In summer episodes, photochemistry can produce peroxy radicals which convert NO to NO_2 without consumption of ozone. This can lead to elevated NO_2 to NO_x ratios in summer, which have to some degree been obscured by data averaging to produce Figure 6.4. The effect on the general shape of Figure 6.4 is small, particularly as the higher NO_x concentrations tend to occur in the winter months.

6.4 UK Concentrations of NO and NO_x

Measurements of NO_x species at UK sites derive from two kinds of measurement. These are as follows:

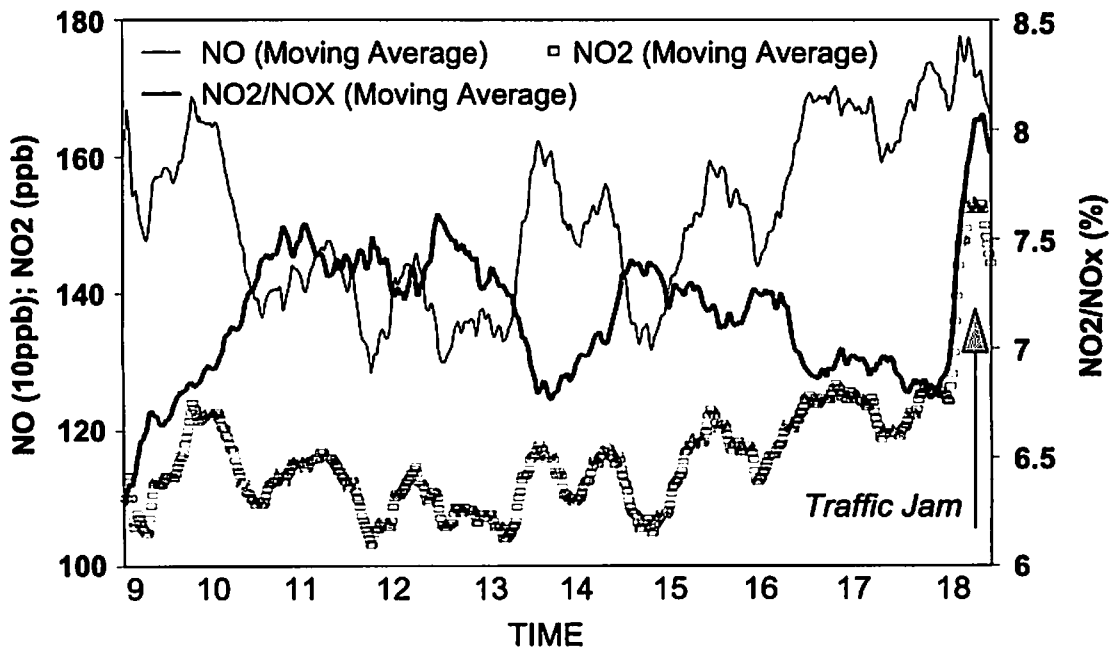

Figure 6.3 Measurements of NO and NO_2 in a Birmingham road tunnel.

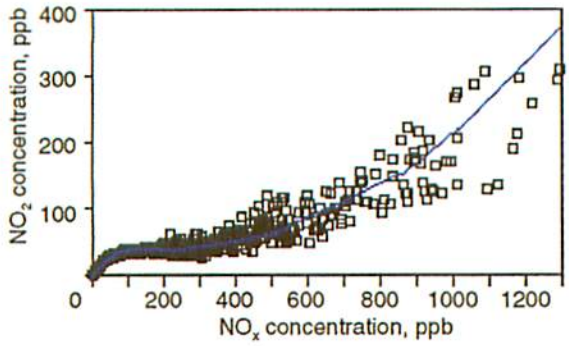

Figure 6.4 Hourly average NO_2 and NO_x concentrations at Exhibition Road, London.

(i) Continuous Chemiluminesence Analysers

These depend upon the reaction of nitric oxide with ozone, itself generated within the instrument, leading to light emission which is measured. The instruments measure NO concentrations directly without known interferences, and NO_2 concentrations by difference between NO_x and NO. NO_x is measured after passage of the air through a heated molybdenum converter in which NO_2 is converted to NO. Unfortunately, some other NO_y compounds such as PAN and HNO_2 are also converted to NO in the instrument and a positive interference in the NO_2 measurement occurs. This is probably of small significance at urban sites under most atmospheric conditions, but could be important in rural measurements.

The locations of national network sites are shown in Figure 6.5. The majority of these are at urban locations and form part of the Automatic Urban Network which resulted from an amalgamation of the Enhanced Urban Network with various statutory and *ad hoc* monitoring activities. The former Enhanced Urban Network stations (Birmingham East, London Bloomsbury and all sites with the word "Centre") are located in urban background locations such as city centre shopping areas and pedestrianised streets where they experience high central urban pollution concentrations, but are not heavily influenced by industry or an individual major road. The former EU Directive Network sites (Glasgow, Billingham, Manchester, Sheffield, Walsall, Bridge Place and West London) are positioned in accordance with the NO_2 Directive to sample within heavily polluted areas. Cromwell Road is a roadside site and Stevenage (now closed) a sub-urban site influenced by the A1(M) motorway. There are also four rural sites operated as part of the rural ozone/NO_x network (Strath Vaich, Glazebury, Harwell and Lullington Heath).

(ii) Diffusion Tube Measurements

These measurements are made using much simpler monitoring devices which require one or two weeks to collect sufficient sample for analysis and hence provide only long term average measurements. Diffusion tubes are cheap and can be deployed at large numbers of sites. They have the disadvantage, however, of being imprecise and tending to over-read in a site-specific manner.

A detailed intercomparison of diffusion tubes with chemiluminescence instruments (Campbell *et al*, WSL report LR 893) has quantified this tendency for diffusion

Figure 6.5 National network sites, measuring NO_x up to 1995.

tubes to over-read; on average diffusion tubes gave results about 30% higher, but the factor was extremely variable and at some sites the two techniques were in good agreement. This is consistent with the observations that wind can cause turbulence at the tube inlet which reduces the effective diffusion length leading to more rapid NO_2 uptake (Gair and Penkett, 1995). This effect is dependent on wind speed and thus on the specific siting of the tube. Because the effect is site-dependent, the data are presented uncorrected.

In principle diffusion tubes measure only NO_2, however recent work by Heal and Cape (1997) suggests that in urban areas the diffusion tubes measure some NO as well as NO_2. However, because of their cheapness, diffusion tubes are ideal for deploying in large numbers to map spatial distributions. They are, however, inherently less accurate than chemiluminescent monitors and cannot generate information directly on hourly average concentrations essential to evaluation of health risks.

Data are presented in this report from two networks of diffusion tubes. The first are located at rural sites and have been operated since 1987. They are thus useful for indicating temporal trends in concentration in rural areas. The second network comprises approximately 1100 monitoring locations within urban areas, which broadly divide into kerbside, intermediate and background locations. Data are available from surveys conducted in 1993 and 1994.

6.4.1 Measurements of NO and NO_2 from National Network Sites

Data covering the period from 1988 to 1994 for both NO and NO_2 appears in Appendix 5, Tables A5.1 and A5.2. These are the most reliable datasets for absolute

concentrations and show for NO_2 annual means varying from about 1 ppb at Strath Vaich in the north of Scotland to 9-10 ppb at Ladybower in northern England where there is a significant pollution influence from power station plumes, to about 9 ppb at Lullington Heath on the Sussex coast. 98th percentile concentrations exceed 30 ppb at both Ladybower and Lullington Heath, whilst being only about 8 ppb at Strath Vaich.

Sites such as Glasgow, Manchester, Walsall, Billingham and Sheffield were established as part of the NO_2 Directive Network designed to monitor some of the more polluted locations in the country, and in recent years where there has been an overlap in the monitoring periods, these have tended to show higher annual mean concentrations than many of the former Enhanced Urban Network sites positioned at central urban background locations, which show considerable similarities in their annual means (e.g. Swansea 23 ppb; Southampton 23 ppb; Leicester 23 ppb; Hull 24 ppb; Liverpool 26 ppb; Bristol 24 ppb; Birmingham (Central) 24 ppb in 1994). Bridge Place in central London showed a higher annual mean (34 ppb) in 1994 and Cromwell Road, a roadside site in London, showed the highest annual mean (44 ppb) and 98th percentile (90 ppb) of all these sites in 1994. The elevation in NO_2 at Cromwell Road is, however, quite modest compared to the elevation in nitric oxide; Cromwell Road saw an annual mean of 161 ppb in 1994 which may be compared with 37 ppb at Bridge Place and 39 ppb in west London in the same year. Interestingly, though, maximum hourly nitric oxide concentrations are not so obviously different between Cromwell Road and the background sites in London.

Maximum hourly concentrations of NO_2 exceed 200 ppb at many of the urban sites and have on occasion exceeded 300 ppb at some sites. The most notable NO_2 pollution episode was in December 1991 in London, when the maximum hourly average concentration of NO_2 at Bridge Place reached 423 ppb. An important facet of the pollution episode was that NO_2 concentrations at the three London sites, Bridge Place, West London and Cromwell Road tracked one another closely for several days (Bower *et al* 1994).

6.4.2 Estimated Spatial Distribution of NO_2 Across the UK

In the Third Report of this Review Group (PORG, 1993), attention was drawn to maps of NO_2 concentrations derived from diffusion tube results and population data from surveys in July to December of the years 1986 and 1991. A similar mapping exercise using a comparable technique has been used for 1994 and the results appear in Figure 6.6. This map is calculated from a rural NO_2 field calculated from network measurements, together with land cover information and NO_x emissions from major roads from the National Atmospheric Emissions Inventory. The following equation is used.

NO_2 = rural NO_2 + 21.3URBLC + 0.0017NO_x emissions

where URBLC = proportion of land cover that is urban in each 5 kilometre grid square and NO_x emissions = NO_x emissions from major roads (in tonnes per 5 km square)

As might be expected, the general spatial distribution is very similar to that for 1986 and 1991 and is dominated by proximity to emissions from road traffic. In general, the magnitude of concentrations appears to lie somewhere between that observed in 1986 and 1991, there having been a substantial increase between the two years. Rural areas in much of Scotland, some of Northern Ireland, Wales and southwest England have rural concentrations below 4 ppb. However, the major part of England, excluding the southwest and north, have concentrations exceeding 8 ppb with many rural areas in the range 12-16 ppb.

6.4.3 Urban Nitrogen Dioxide Diffusion Tube Survey

As mentioned above, the urban survey covered over 1100 sites. In the 1993 study (Stevenson and Bush, 1993) a total of 880 sites provided a valid annual average for the year. In each local authority area, measurements were undertaken at one kerbside, one intermediate and two urban background sites.

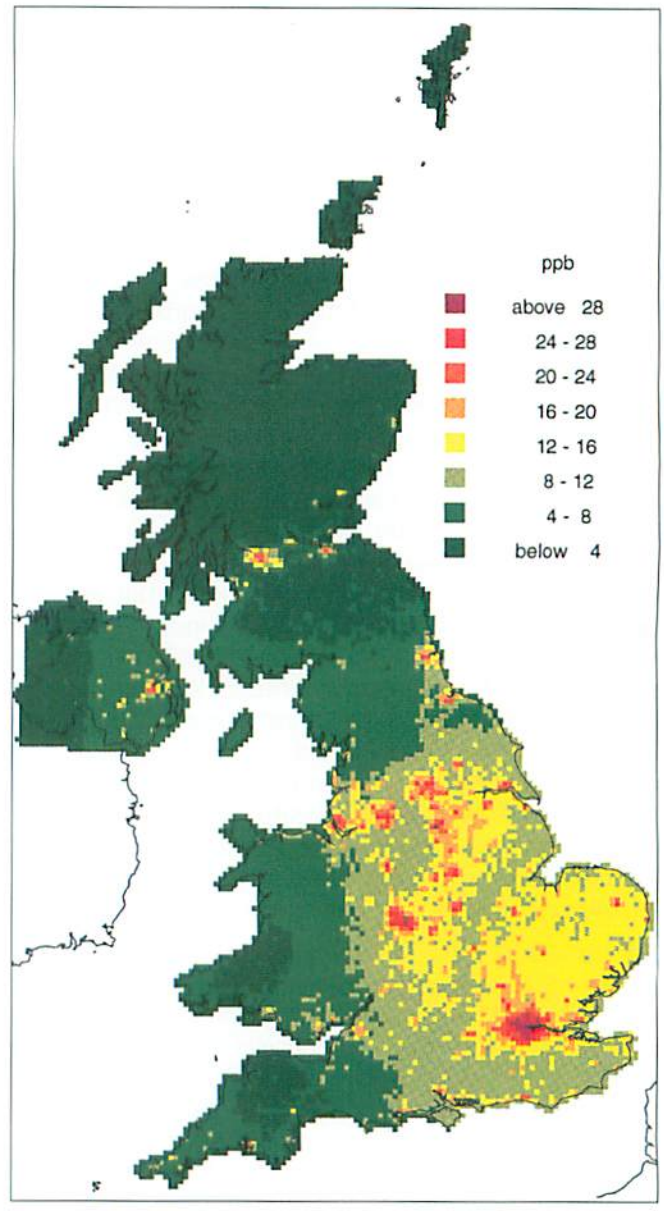

Figure 6.6 1994 estimated annual mean NO_2 concentration, from rural NO_2, land cover and roads data. Data supplied by John Stedman at NETCEN (AEAT).

Table 6.2 Summary of statistically significant trends in NO_x, at sites with at least five years of measurements, Central London is highlighted with more than ten years of measurements.

Site	Annual Parameter	Start Year, 19##	End Year, 19##	Slope	Slope Error	Units	R
Central London	**98th percentile**	**77**	**94**	**+6.0**	**3.0**	**ppb yr^{-1}**	**+0.55**
Cromwell Road	mean	90	94	-15.0	5.0	"	-0.86
Cromwell Road	98th percentile	90	94	-60.0	20.0	"	-0.87
West London	mean	87	94	-5.0	2.0	"	-0.72
Glasgow	98th percentile	90	94	-26.0	7.0	"	-0.91
Walsall	mean	87	94	-2.9	1.0	"	-0.78
Walsall	98th percentile	87	94	-23.0	6.0	"	-0.84
Billingham	mean	87	94	-1.5	0.6	"	-0.73

The measurements indicated that overall, kerbside site concentrations were higher than measurements at background and intermediate sites by a factor of approximately 1.6.

Intermediate concentrations were only marginally higher than background sites taken as an overall average. The highest intermediate and urban background concentrations were found in parts of the northwest and Yorkshire.

Lowest concentrations were generally found in the less heavily populated areas. One perhaps surprising finding was that the spatial pattern of NO_2 concentrations determined from this survey was significantly different from that determined in previous studies in that the highest concentrations were not recorded in the London area. However, the number of sites and site locations were entirely different from previous national NO_2 studies in the UK and this feature needs to be kept under review.

6.5 Temporal Trends in NO and NO_2

Whereas for ozone, inter-annual variability in peak and mean concentrations is strongly influenced by the occurrence of anticyclonic weather conducive to ozone formation, concentrations of NO_x are influenced mainly by the total emissions, and the ability of the atmosphere to disperse the pollutant and hence reduce the concentrations. Long-term trends in concentration may be difficult to discern because of year to year variations in the weather which influence dispersion within the atmosphere. Thus, trends in concentration reflecting changes in emissions may only be clearly recognised in quite long runs of data. Emissions of NO_x from road traffic, which have the greatest influence on ground-level concentrations, increased appreciably prior to 1989 over a period in which few sites were carrying out measurements. Since that time there has been a decrease in emissions of 22% between 1989 and 1994.

6.5.1 Automatic Monitoring Sites

A summary of NO_x trend data for those sites having eight or more years data appears in Table 6.2. All of the sites with five to eight years data have shown decreases in NO_x concentration to 1994. Data from the heavily traffic-influenced Cromwell Road site appear in Figure 6.7. This shows a clear downward trend in NO_x, but this may be accounted for in part by a reduction in traffic volumes in recent years on this road. The only site with a longer run of data, Central London, actually a compilation of data from three sites of similar characteristics, shows an increase in 98th percentile NO_x concentration between 1977 and 1994. Both of the observed trends are consistent with the emissions inventory data and show that recent application of modern emission controls to motor vehicles has had a beneficial impact on air quality. In Sweden, where catalytic converters were introduced earlier than in the UK, a decrease of about 30% in NO_2 has been observed in urban areas.

Trends in nitrogen dioxide are more difficult to discern and far more complex to interpret than for NO_x since NO_2 is not a directly emitted primary pollutant, but depends upon atmospheric processes for its formation. Data from sites with five or more years of measurement appear in Table 6.3 and all show a small downward trend in NO_2. For the majority of sites, this trend covers the period from 1987-1994 or 1990-1994, with one site, Cromwell Road, covering from 1982-1994. Our Third Report (PORG, 1993) noted that upward trends in NO_2 shown in rural data were not reflected in trend measure-

Table 6.3 Summary of statistically significant trends in NO_2, at sites with at least five years of measurements, Cromwell Road is highlighted with more than ten years of measurements.

Site	Annual Parameter	Start Year, 19##	End Year, 19##	Slope	Slope Error	Units	R
Cromwell Road	**98th percentile**	**82**	**94**	**-6.0**	**2.0**	**ppb yr^{-1}**	**-0.71**
West London	mean	90	94	-1.1	0.2	"	-0.93
West London	98th percentile	87	94	-5.0	2.0	"	-0.74
West London	98th percentile	90	94	-3.7	0.6	"	-0.97
Glasgow	mean	87	94	-0.7	0.2	"	-0.78
Glasgow	98th percentile	87	94	-2.0	0.7	"	-0.78
Walsall	mean	87	94	-0.6	0.2	"	-0.73
Walsall	98th percentile	87	94	-1.3	0.5	"	-0.72
Billingham	mean	87	94	-1.0	0.1	"	-0.95
Billingham	98th percentile	87	94	-3.0	0.5	"	-0.91
Billingham	mean	90	94	-1.3	0.3	"	-0.94
Billingham	98th percentile	90	94	-4.0	1.0	"	-0.92

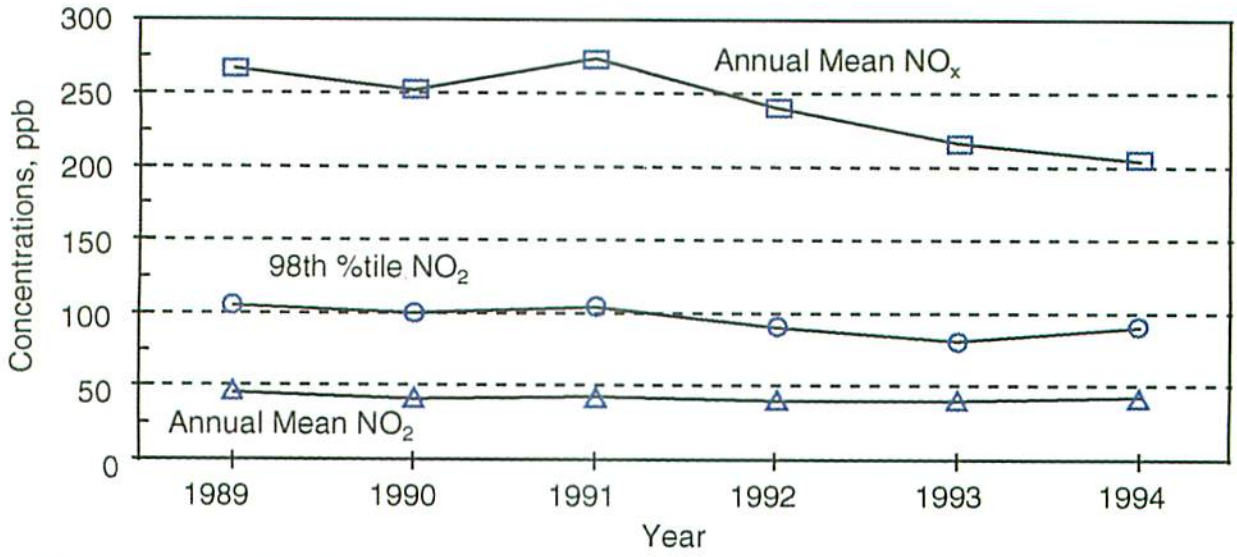

Figure 6.7 Annual mean NO_x, NO_2 and 98th percentile NO_2 measurements at Cromwell Road, London.

ments from traffic-saturated city centre sites. It should be noted that the data in Table 6.3 come from central urban or industrially-influenced sites and thus may not be representative of trends in rural areas, which are more readily elicited from the rural diffusion tube data.

Our Third Report (PORG, 1993) included a time series of markedly increasing concentrations of NO_2 at the rural Bush Estate site in southern Scotland which showed an increase in the annual mean NO_2 concentration of about 30% over the period 1988 to 1991. An extension of that dataset to 1993 shows a continued increase in NO_2 at a rate of approximately 0.4 ppb per year over the six years (see Figure 6.8). The steepest increase appears to be in the late 1980's with a rather flatter trend from 1991 to 1993. Sulphur dioxide has decreased, at approximately 0.07 ppb per year over the six years and the NO_2 to SO_2 ratio has changed from 2:1 in the 1980's to 3:1 at present. This exemplifies a trend which has taken place in UK rural air for the once predominant sulphur dioxide to be overtaken in concentration by nitrogen dioxide, which is now the more abundant of the two gases at most rural locations.

6.5.2 Rural Diffusion Tube Measurements

There are a number of rural sites at which almost continuous runs of data are available from 1987, or earlier in one case. Data were collected from 1987 to 1991 by the Harwell Laboratory. Warren Spring Laboratory also collected NO_2 diffusion tube data at some of the same sites starting between 1985 and 1987, and also brought in additional sites starting in 1991. NETCEN have integrated the two datasets, having established comparability between measurements obtained by the two laboratories. The longest run of data is for Barcombe Mills in Sussex shown in Figure 6.9. The data show a very clear seasonal variation, and like the continuous urban sites, show a decline in concentrations from about 1989 onwards. The data from this network which covers rural sites in England, Wales and Scotland is fairly consistent in showing a modest decline in concentrations over the period 1987 to 1995, which corresponds with the emissions inventories. Some of these sites are particularly likely to be influenced by power station emissions which have been declining from a peak in 1987 (see Table 6.1).

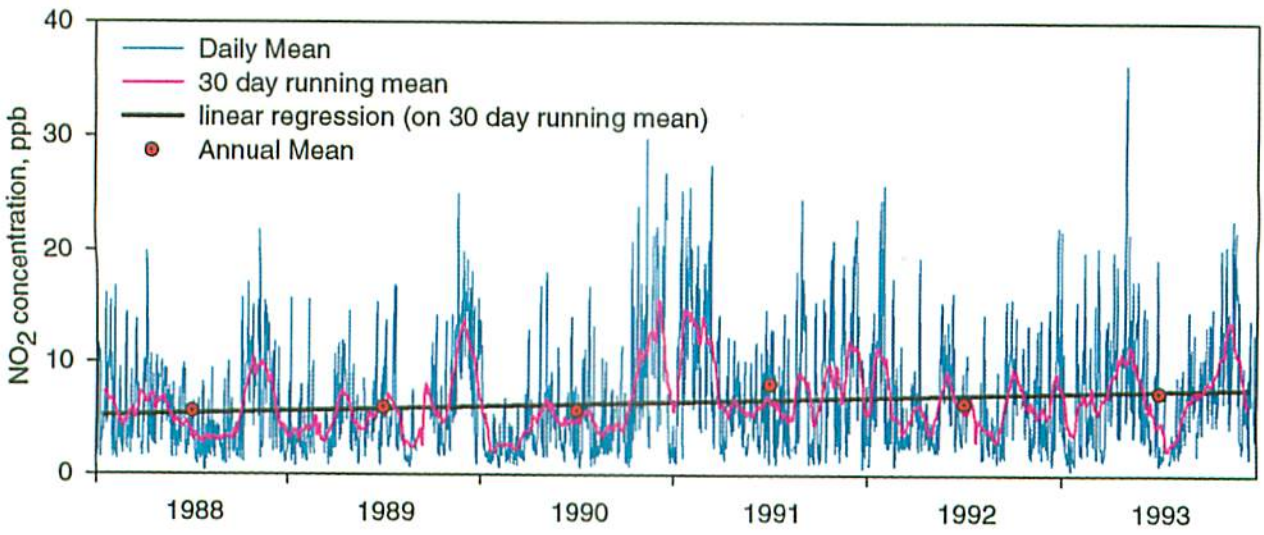

Figure 6.8 NO_2 concentrations at Bush from 1988 to 1993.

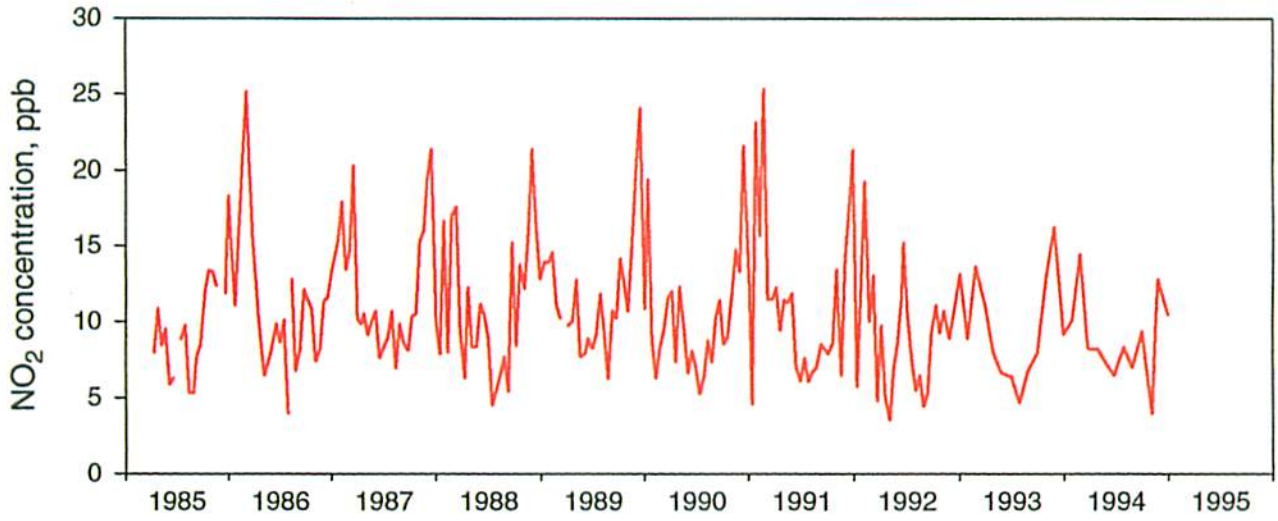

Figure 6.9 NO_2 diffusion tube survey time series for Barcombe Mills, Sussex, March 1985 - 1994.

6.6 Oxidised Nitrogen Deposition in the UK

The gaseous oxides of nitrogen in the atmosphere over the UK are removed by chemical reaction, deposition and advection from the UK coastline (removal by wind). The chemical reactions transform emissions of NO to NO_2 very rapidly with O_3 as the oxidant. Further oxidation of NO_2 occurs directly to HNO_3 by reaction with OH or via the NO_3 radical, as described in Chapter 2. The deposition processes lead to efficient scavenging of aerosol NO_3^- and HNO_3 by precipitation. The wet deposition is monitored by networks of precipitation collectors which are used to estimate wet deposition using the precipitation fields as described in RGAR (1997). Annual wet deposition currently removes 110 kt N over the UK representing just 14% of emissions.

The wet deposition is largest in the high rainfall uplands of Wales, Northern England and West Scotland, and smallest in East Anglia and the SE of England. Dry deposition by contrast is largest in the areas of highest NO_2 concentration.

Dry deposition of NO_2 onto vegetation and soil is largely regulated by stomatal uptake, there being very little cuticular uptake of NO_2 (Hargreaves *et al,* 1991; Hanson *et al,* 1988). This results in terrestrial inputs of 40 kt N annually in the UK or 5% of emissions by dry deposition. In addition to emissions within the UK, some NO_x is advected into the country from Continental Europe and has been estimated at 60 kt N by EMEP. The total deposition of oxidised nitrogen within the UK of 150 kt N represents just 19% of emissions, the remainder being advected out of the country, largely to the east by the prevailing westerly winds. The annual average atmospheric boundary layer budget over the UK for oxidised nitrogen is illustrated in Figure 6.10 for the period 1992 to 1994 (RGAR, 1997).

Although the deposition of reduced nitrogen (NH_x) is outside the remit of this report, the current interest in nitrogen effects on eutrophication of natural and semi-natural ecosystems has become an important issue and may well contribute to the setting of critical loads for nitrogen deposition. It is of interest therefore to compare the relative contribution of oxidised and reduced nitrogen to the total deposition of nitrogen in the UK. For the period 1992-1994, the oxidised nitrogen deposition represents 45% of the total, the remainder being reduced nitrogen, even though reduced nitrogen emissions are less than half of oxidised nitrogen emissions. The inputs are therefore partitioned fairly uniformly between oxidised and reduced nitrogen largely because reduced nitrogen has a much shorter atmospheric lifetime and transport distance. Oxidised nitrogen therefore has a much larger "environmental footprint" on a continental scale rather than reduced nitrogen which is more of a local or regional problem.

6.7 Comparison of NO_2 Concentrations with Air Quality Standards

At the time of writing, the Expert Panel on Air Quality Standards had yet to recommend a UK standard for nitrogen dioxide, (they have now recommended a standard of 150 ppb as an hourly average, EPAQS, 1996). The European Union has set a limit value and

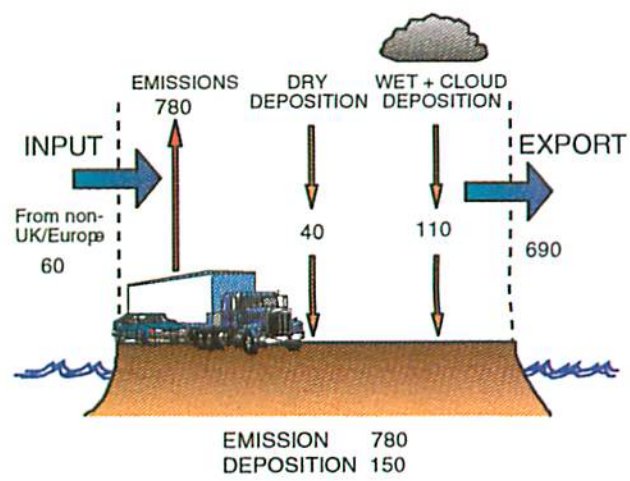

Figure 6.10 Budget for the deposition and emission of oxidised nitrogen in the UK, estimate for the period 1992-1994.

Table 6.4 EPAQS, EU, WHO and UNECE guidelines for NO_2.

Guideline set by:	Description	Criteria	Value	
			ppb*	µg m^{-3}
EPAQS	Health standard	Hourly mean	150	282
European Union		Calendar year:		
	Limit value	98 %tile of hourly means	106	200
	Guide value	98 %tile of hourly means	71.6	135
	Guide value	50 %tile of hourly means	27	50
World Health Organisation	Health guideline	Hourly mean	*106*, (212)	*200*, (400)
Values in italics recently revised from those shown in brackets	Health guideline	Daily mean	80	150
	Vegetation guideline	4 - hourly mean	50	95
	Vegetation guideline	Annual mean	*21*, (16)	*40*, (30)
United Nations Economic Commission for Europe	Vegetation guideline (critical level) also applies to NO_x	Annual mean	15	29

* at 25°C and 1013 mb

guide values for nitrogen dioxide and the World Health Organisation recommends human health-based guidelines. Additionally, vegetation guidelines have been set both by the WHO and United Nations Economic Commission for Europe. These are shown in Table 6.4, whilst Tables A5.3 and A5.4 in Appendix 5 detail the exceedences of these standards over the period 1988-1994. As noted in our Third Report, the EC Directive limit value was exceeded at one urban background site (London Earls Court) in 1989, but this was shown by a detailed investigation to be due to unusual interference from local sources. Additionally, the kerbside site at London, Cromwell Road exceeded the limit value in 1989 with a 98th percentile at 105 ppb. Such exceedences will become less likely as nitrogen dioxide concentrations diminish. EU guide values for nitrogen dioxide are widely exceeded at city centre sites and considerable further emissions reductions will be required to remedy this situation.

In 1995 the World Health Organisation recommended a halving of its one hour guidelines for nitrogen dioxide from 400 µg m^{-3} (210 ppb) to 200 µg m^{-3} (105 ppb). The latter is a concentration which is still exceeded occasionally at central urban locations. Thus, whilst NO_2 concentrations are decreasing, the target concentrations for acceptable air quality have also fallen and are still exceeded.

6.8 Nitric Acid and Particle Nitrate

Atmospheric oxidation of nitrogen dioxide leads to the formation of nitric acid, HNO_3. This compound exists in the atmosphere as a vapour, but can be rapidly converted to nitrate particles either by reaction with ammonia, which is reversible, or by reaction with other particles such as sodium chloride.

$$HNO_3 + NH_3 \leftrightarrow NH_4NO_3$$
$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$$

Because of this ready inter-conversion of nitric acid and nitrate particles, the EMEP network (Schuag *et al*, 1992, 1993, 1994) measures nitrate as the sum of particle nitrate and nitric acid. Data from UK sites in recent years appears in Figure 6.11. Generally, under UK atmospheric conditions with an abundance of ammonia, the partition of nitrate between nitric acid and particles is strongly in favour of the particulate form.

6.9 Nitrous Acid

A further oxyacid of nitrogen, which is present in the atmosphere at similar concentrations to nitric acid, is nitrous acid, HONO. The atmospheric chemistry of this species is described in Chapter 2.

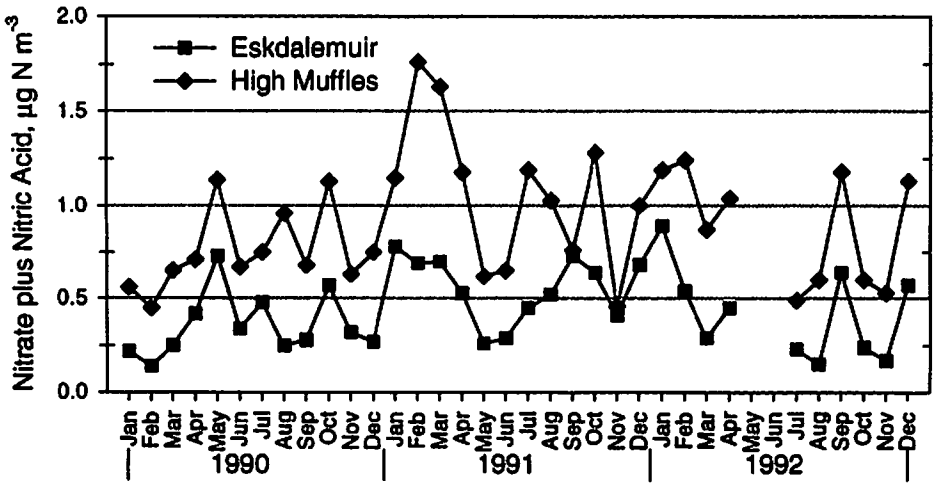

Figure 6.11 The sum of particle nitrate and nitric acid at the UK EMEP monitoring stations, High Muffles and Eskdalemuir.

Figure 6.12 shows data collected in suburban Birmingham where the behaviour of HONO can be well explained by a model including ground surface formation of HONO from NO_2, HONO photolysis and reformation from the NO + OH reaction (Harrison *et al* 1996b).

Figure 6.13 gives a breakdown of NOy speciation on a polluted day at Weybourne, Norfolk in the autumn of 1996 (Penkett *et al* unpublished) as a function of time of day. The first and third sample, collected mainly in hours of darkness, show no significant NO and considerably more HONO than the daytime (0800 to 1600) sample. It is notable that a small proportion of NO_y remains unaccounted for in all samples and is probably explained in part by organic nitrates which were not analysed.

6.10 The Effects of NO_2 on Human Health

The Advisory Committee on the Medical Aspects of Air Pollution Episodes (MAAPE) report on Oxides of Nitrogen was published in 1993 and provided a detailed review of the literature available up to about mid 1992, (Dept. of Health, 1993). This short review outlines the major developments since then.

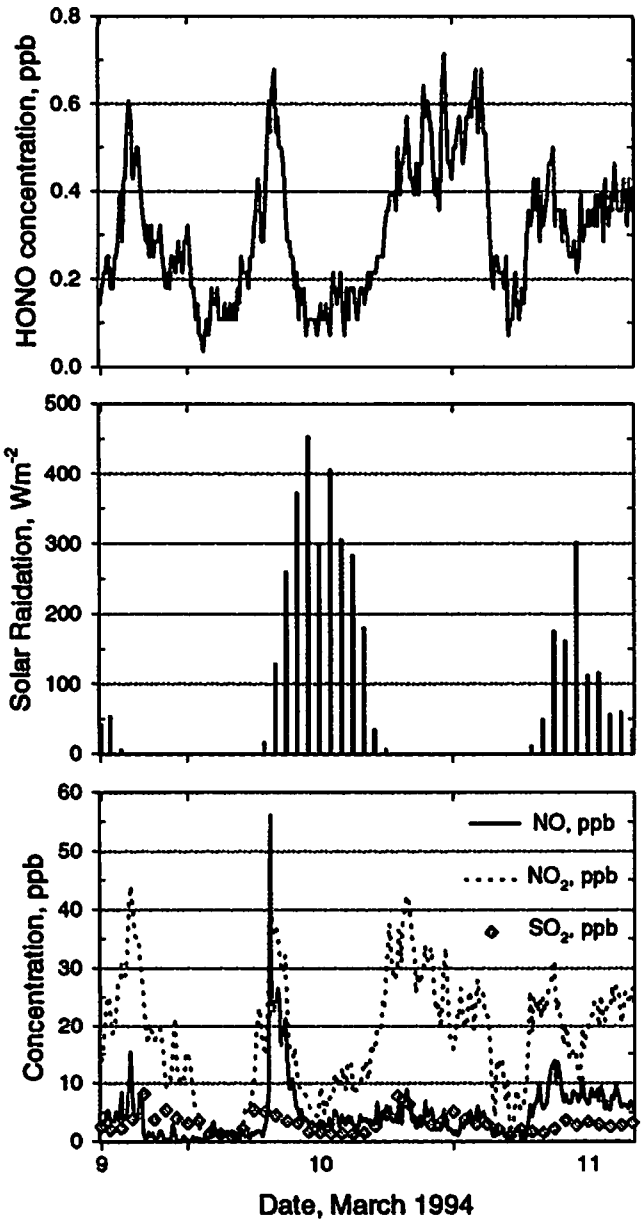

Figure 6.12 Measurements at a sub-urban site in Birmingham.

6.10.1 Studies of the Mechanism of Action of Nitrogen Dioxide

Like ozone, nitrogen dioxide is an oxidising agent and can induce lipid peroxidation of cell membranes and extracellular lipids via the formation of free radicals (Guidotti, 1978: Menzel, 1976: Mustafa & Tierney, 1978). Conversion to nitrite and then nitrate follows absorption (Postlethwait & Mustafa, 1981). The formation of lipid peroxides leads to a cascade of inflammatory mediators and a number of cytokines are released (Devalia *et al* 1993). Inflammation of the airway lining follows with an increase in capillary permeability and a leak of protein into the intercellular space. If the inflammation is marked, protein may leak from the surface of the epithelium.

A study of adult asthmatic subjects has shown that more than 70% of inhaled nitrogen dioxide is absorbed. This percentage is maintained during exercise and thus the dose absorbed per unit time increases with the ventilation (Overton & Miller, 1968). Many of the cells of the conducting airways are ciliated. A number of studies have shown that nitrogen dioxide inhibits ciliary activity (Devalia *et al*, 1990). Not all studies are in agreement on this and there is as yet no consensus on the effects of ambient concentrations of nitrogen dioxide on either ciliary function or clearance of mucus.

Long term exposure to concentrations of nitrogen dioxide of greater than about 1 ppm have been shown to produce a marked inflammatory response in the airways of experimental animals (Chang *et al*, 1988). The inflammatory response may be secondary to cellular damage and the Clara cell has been identified as perhaps the most likely initial site of damage (Kawakami *et al*, 1989). Clara cell damage has been monitored by measurement of the Clara cells specific protein CC10 in lavage fluid (Barth *et al* 1994). Clara cells produce surfactant as do Type II alveolar cells. The effect of nitrogen dioxide on the production and properties of surfactant has been studied: increased production, reduced release and a reduction in the capacity of the secretion to lower the surface tension of water have been recorded (Muller *et al*, 1994).

It has been suggested that exposure to nitrogen dioxide may reduce the capacity of the respiratory tract to resist infection: see below; support for this has come from *in vivo* and *in vitro* studies. The reported *in vivo* studies are difficult to interpret as both high concentrations of nitrogen dioxide and heavy challenges by pathogenic organisms have been employed. The following effects have been demonstrated:

a. Reduction in defence against bacterial and viral challenge (Ehrlich, 1966: Goldstein *et al* 1973: Jakab, 1988)

b. Depression in macrophage antibacterial function (Davis *et al*, 1992: Acton & Myrvik, 1972: Greene & Schneider, 1978).

Interestingly, a study of human alveolar macrophages

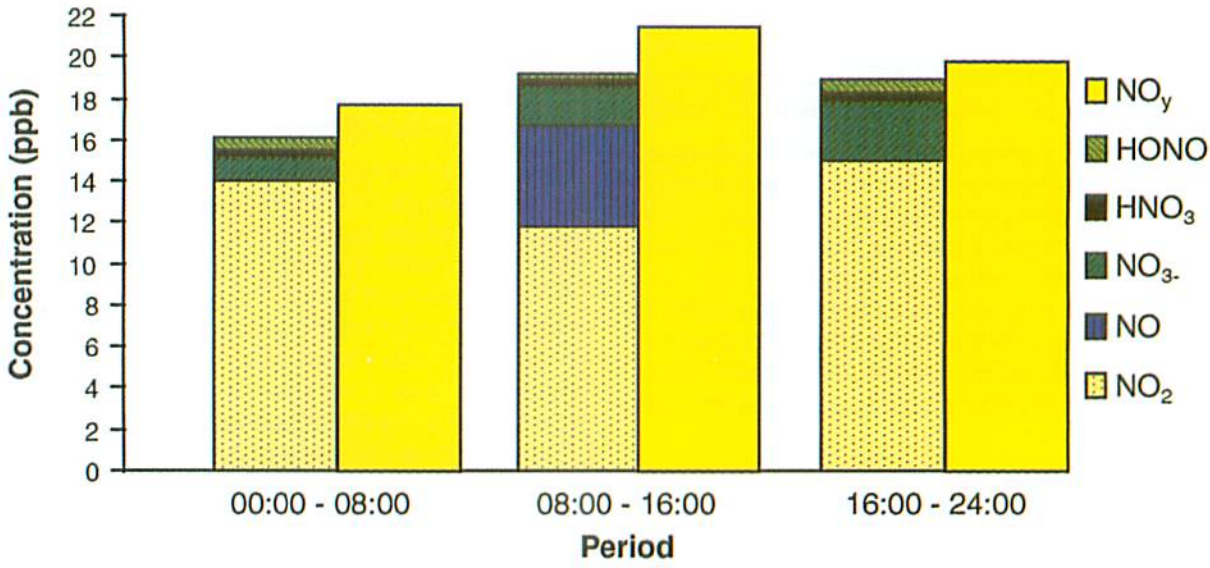

Figure 6.13 Budget of NO_y on a polluted day at Weybourne, Norfolk (WAOWE94, 2/11/94, Julian day 306).

recovered by lavage after exposure of subjects to a range of concentrations of nitrogen dioxide (5 -15 ppm for 3 hours) showed little effect on the capacity of the cells to release IL-1 after challenge with influenza virus (Pinkston *et al* 1988). A similar study (Frampton *et al* 1989) revealed a marked intersubject variation in effects on macrophages.

It has been suggested that nitrogen dioxide is carcinogenic. No convincing evidence that this effect is likely in man has yet been produced (Witschi, 1988: Ichinose, 1991).

Volunteer studies of the effects of nitrogen dioxide

Exposure of normal and asthmatic volunteers to concentrations of nitrogen dioxide in excess of 1 ppm have produced variable results. Early studies (Bell *et al* 1976) showed that exposure to 5 and 7.5 ppm produced an increase in airway resistance. A later study by Linn *et al* (1985) showed no effect on lung function either in normal or asthmatic volunteers on exposure to 4 ppm for 75 minutes. At concentrations between 0.5 and 1 ppm a number of workers have, similarly, failed to demonstrate effects on lung function in normal subjects. A detailed compilation of the results of these studies is presented in the MAAPE report on Oxides of Nitrogen (Dept. of Health, 1993). Studies in asthmatic subjects at concentrations between 100 and 1000 ppb have generally also failed to demonstrate effects. Some decrement in FEV1 has been shown on exposure to 300 ppb nitrogen dioxide;(Bauer *et al*, 1986: Roger *et al*, 1985) again a detailed list of results is provided in the MAAPE report.

Studies in asthmatic subjects have demonstrated that exposure to nitrogen dioxide can increase the response to bronchoconstrictor agents. Orehek (Orehek *et al*, 1976) demonstrated that exposure to 100 ppb of nitrogen dioxide increased the response of asthmatic subjects to methacholine. Other workers have failed to reproduce this result and the Orehek study has not been weighted heavily by expert groups considering the effects of nitrogen dioxide (WHO, 1995). More recently, Devalia *et al* (1994), have reported that exposure of mildly asthmatic patients for 6 hours to 200 ppb of sulphur dioxide and 400 ppb nitrogen dioxide increased sensitivity to house dust mite allergen. Similar effects have been reported by others (Tunnicliffe *et al*, 1994).

In summary, exposure of volunteers, both normal and asthmatic, to ambient concentrations of nitrogen dioxide has not demonstrated significant changes in standard indices of lung function. There is some suggestion that the dose-response relationship for nitrogen dioxide may be discontinuous though the reasons for this are unclear. That nitrogen dioxide, at ambient concentrations, can enhance the response to allergen seems reasonably established.

Epidemiological studies

A large number of studies of the effects of nitrogen dioxide on public health have been published. In most studies nitrogen dioxide is only one of the pollutants to which individuals have been exposed and some difficulty has been met in attempting to sort out which pollutants have the greatest effects. In a number of studies, particles and ozone have been demonstrated to have a more significant effect than nitrogen dioxide. Almost no information on individuals' exposures is available. The reported studies fall into a number of groups.

Studies of the effects of day to day variations in concentrations of nitrogen dioxide and lung function and symptoms amongst a panels of subjects

The studies of Hoek and Brunekreef are perhaps the best known in this group. The authors have followed day to day variations in concentrations of a range of pollutants and have related these to the day to day state of a panel of subjects. In a series of studies reported in 1993 and 1994, nitrogen dioxide was observed to have no effect in two studies and to have a small but significant effect in the third (Hoek *et al*, 1992, 1994: Roemer *et al*, 1993). In a study in London no relationship was demonstrated between daily concentrations of nitrogen dioxide and symptoms in a group of subjects suffering

from allergic diseases of the upper respiratory tract though variations in ozone concentrations were shown to have an effect (Fitzharris *et al*, 1994)

Other studies have concentrated on the relationship between day to day variations in concentrations of nitrogen dioxide and hospital admissions for the treatment of asthma attacks. Rossi *et al* (1993), demonstrated a significant correlation between concentrations of nitrogen dioxide and hospital visits. Studies in the UK have demonstrated a relationship between indices of lung function and day to day variations in nitrogen dioxide amongst asthmatic patients in summer but not in winter (Taggart, *et al*, 1994: Taggart, Higgins *et al*, 1994). Interestingly, the same authors showed that responsiveness to methacholine, in summer, varied with ambient concentrations of nitrogen dioxide (Taggart *et al*, 1994). In this study ambient concentrations of nitrogen dioxide were low and the results give support to those of Orehek mentioned earlier. A relationship between symptoms in asthmatic patients and concentrations of nitrogen dioxide has been reported by Tzanakis and supported by the work of Diakite (Tzanakis *et al*, 1993: Diakite *et al* 1994).

The effects of variations of monthly average concentrations of nitrogen dioxide and levels of ill-health (occurrence of bronchitis and severity of asthma) have been studied by Abbey: no relationship was found (Abbey, 1994).

Studies of lung function and ill-health in communities characterised by differing long term concentrations of nitrogen dioxide

In a carefully conducted study of three Alpine regions, Schmitzberger (Schmitzberger *et al*, 1993) reported an inverse relationship between indices of lung function and long term average concentrations of nitrogen dioxide. This finding has been supported by those of the SAPALDIA STUDY in Switzerland (Leuenberger *et al*, 1994). Here, adult lung function was found to be inversely related to long term average concentrations of NO_2, SO_2, TSP and pm10. Cross sectional studies have also revealed an increased level of atopy and increased bronchial responsiveness in polluted regions of France (Charpin *et al* 1994: Forastiere, 1994).

Effects of exposure to indoor air pollution characterised by raised concentrations of nitrogen dioxide

A number of studies have looked at the effects of indoor exposure to nitrogen dioxide and other products of combustion of various cooking and space-heating devices. A detailed review of the earlier studies was provided in the MAAPE report on Oxides of Nitrogen. In that review the meta-analysis of Hasselblad *et al*, 1992, was considered in detail and will not be reviewed again here. This and other studies were also reviewed in 1994 by a WHO Expert Group (WHO, 1995) and the following assessment produced:

"From the epidemiological studies, children 5 to 12 years old are estimated to have a 20% increased risk for respiratory symptoms and disease for each increase of 28.3 µg/m^3 (0.015 ppm) NO_2 (2 week average) where the weekly average concentrations are across the range of 15 to 128 µg/m^3 (0.008-0.065 ppm) or possibly higher"

Perhaps the most important recent study in this area is that reported in early 1996 by Jarvis *et al*. In this study a significant relationship between depression of lung function and the occurrence of respiratory symptoms was discovered in women who use gas cookers. The presence of an open gas fire added to the effects. These findings support those of Ostro *et al* (1993), which indicated that the use of gas cookers was related to an increased use of medications by asthmatic individuals.

The interpretation of studies of the effects of exposure to gas cookers is complicated by the greater significance of the demonstrated associations with the presence of gas cookers than with concentrations of nitrogen dioxide. It is possible that other products of combustion, water vapour and aldehydes, may be playing a role. Further studies are needed to clarify this picture.

Studies of air pollution episodes characterised by raised concentrations of nitrogen dioxide

The London air pollution episode of 1991 has been studied in detail by Anderson (CLAG, 1997). During the episode concentrations of nitrogen dioxide and Black Smoke were very significantly raised: Maximum Hourly averages: nitrogen dioxide: 423 µg/m^3, Black Smoke: (24 hour average) 228 µg/m^3. Indices of mortality and morbidity for the episode week were compared with those predicted from control weeks, the relative risks (episode week v predicted) are shown in Table 6.5. It will be seen that respiratory mortality was particularly affected during the episode.

6.10.2 Summary

Both acute and chronic exposure to nitrogen dioxide have been demonstrated to have effects on lung function. Though these effects many not be as marked as those associated with ozone and particles they are significant and, from the health standpoint, nitrogen dioxide remains an important air pollutant.

6.11 NO_x Impacts on Vegetation

6.11.1 Critical Levels for NO_x

Assessment of the potential impacts of air pollutants on vegetation for policy purposes is now primarily based on the critical level approach. This section briefly summarises the current critical level for nitrogen oxides, and the basis on which it was assessed, and describes how areas of the UK experiencing NO_x exposures above the critical level have been identified. More details can be found in the reports of the DETR critical levels group (CLAG, 1997), and by Caporn, (1994).

Critical levels for oxides of nitrogen were originally set at the Bad Harzburg workshop in 1988. These were applied only to NO_2, since other oxides of nitrogen were considered to have no adverse effects on vegetation at normal atmospheric concentrations. The two critical levels set in 1988 were 30 µg m^{-3}, based on a one year averaging time, and 95 µg m^{-3} for a four hour period.

Table 6.5 Health impacts of an air pollution episode in London during 1991.

	Relative Risk	(95% CI)
Mortality		
All causes	1.10	(1.02 to 1.19)
All respiratory, all ages	1.22	(0.98 to 1.51)
COPD + asthma, all ages	1.23	(0.90 to 1.68)
Cardiovascular, all ages	1.14	(1.01 to 1.28)
Hospital admissions		
All respiratory, all ages	1.04	(0.96 to 1.13)
COPD + asthma, all ages	1.14	(1.00 to 1.30)
Ischaemic heart disease	1.04	(0.90 to 1.21)
GP consultations		
All lower respiratory, all ages	1.04	(0.98 to 1.12)
All upper respiratory, all ages	1.10	(1.03 to 1.19)
Asthma, all ages	1.14	(0.98 to 1.05)
Cardiovascular, all ages	0.91	(0.78 to 1.05)

Although these levels were derived from experiments and observations with relatively few species, in the absence of further information the values were applied equally to all vegetation. Since 1988 there have been notable developments in the understanding of ecological impacts of low concentrations of NO as well as NO_2 and, in addition, because a greater variety of plant life has been studied it is now possible to consider the comparative sensitivity of different classes of vegetation.

At the UNECE workshop at Egham in 1992 (Ashmore & Wilson (eds.), 1994), greater ecological importance was attached to the long-term critical level over a one year averaging period than the 4-hour level. The value of 30 $\mu g\ m^{-3}$ for the former was retained but this now applies to NO_x, being the sum of NO and NO_2 concentrations in terms of volume mixing ratios (ppb) and expressed as NO_2 in $\mu g\ m^{-3}$. Although only a crude approximation of NO_x, this combined value does go some way towards reflecting increased knowledge of the phytotoxicity of NO, which comes from recent improvements in understanding of the biochemical basis of action and new experimental data on physiological and growth effects.

Oxides of nitrogen are eventually metabolized by the normal pathways of nitrogen metabolism and can potentially contribute to the nitrogen budget of the plant. Accordingly, while under certain exposure conditions the effects of NO and NO_2 are phytotoxic, in other situations they can stimulate growth. At the Egham workshop, such enhancements of growth in semi-natural vegetation were considered adverse effects because of likely changes in inter-specific competition in plant communities, and the possibility of adverse side-effects such as a heightened sensitivity to frost, drought or pests. There is insufficient evidence at present to justify setting different critical levels of NO_x for different classes of vegetation, as exposure to low concentrations (10-40 ppb) of NO_2, or NO_2 plus SO_2, has elicited metabolic or growth responses in a wide range of plant types, including mosses, shrubs, trees, grassland species and crops (Caporn, 1994).

It has been known for several years that combinations of gaseous pollutants often cause greater effects on plants than exposure to the single gases alone. This is particularly true of NO_2 and SO_2 (Ashenden & Mansfield, 1978) but other combinations also frequently cause synergistic (greater than additive) effects. Recent analysis of the effects literature, however, working on the basis that positive and negative responses are equally adverse, indicates that the critical level for NO_x should apply even in the absence of other gases (WHO, 1994).

6.11.2 Mapping Exceedance of Critical Levels of NO_x

A map of estimated NO_x concentration was derived in the same way as the map of NO_2 concentrations (Stedman, 1995). It was calculated from a map of rural NO_2 concentrations; the local source contribution was estimated from the surrogate datasets of NO_x emissions from major roads and land cover statistics. The empirical model of the relationship between these surrogate statistics and measured urban NO_x concentrations was calibrated using monitoring data.

Rural NO_x concentrations were estimated by multiplying the measured NO_2 concentration at acid deposition sites by 1.2, the ratio between annual mean NO_x and NO_2 concentrations measured using a chemiluminescent monitor at the Lullington Heath site for 1994. The mean of the ratio between annual mean NO_x and NO_2 concentrations for the 10 site years, 1991 to 1995 , with at least 75% data capture, at the three ARN sites was very similar at 1.23 (standard deviation = 0.09).

The following equation was used to calculated the map:

$$est\_NO_x = rural\_NO_x + 0.582.us25km + 0.009.NO_x25km$$

where:

est_NO_x is the estimated annual mean background NO_x concentration for 1994 for the 5 km x 5 km grid square (ppb),

$rural\_NO_x$ is the map interpolated from rural NO_2 measurements (ppb) multiplied by 1.2.

us25km is the mean percentage of (urban + suburban) land cover for an area of 25 km^2 centred at the estimation location;

NO_x25km is the total NO_x emission from major road vehicle sources (tonnes per year) within the 25 km^2 area surrounding the estimation location.

The combined urban and rural map derived for NO_x using this methodology (Fig.6.14) shows that the whole of England experiences concentrations of NO_x above 20 µg m^{-3}, with the exception of the far north of the country, and the south-west. In contrast, NO_x concentrations are below 20 µg m^{-3} throughout rural Wales, Scotland and Northern Ireland. High concentrations are also, as expected, associated with centres of population in almost any region of the country.

A substantial proportion of central and southern England experiences concentrations above the critical level of 30 µg m^{-3}, as do many urban and suburban areas. The total land area in exceedance of the critical level for NO_x represents 29% of the UK.

Figure 6.15 shows the areas in exceedance of the critical level overlain with maps showing the percentage land cover of semi-natural vegetation. As explained above, semi-natural vegetation is the vegetation type most likely to experience adverse impacts where the critical level is exceeded. However, the proportion of this land area covered by semi-natural vegetation is mainly minimal (0-5% in the majority of 5 km grid squares), and only 1% of the total UK land area of semi-natural vegetation is in exceedance of the critical level. The large areas of the UK dominated by semi-natural vegetation in Scotland and upland England and Wales mainly experience NO_x concentrations below the critical level. However, there are several small areas where the existence of a high proportion of natural vegetation (around 50%) and NO_x concentrations above the critical level coincide. Notable cases are the central southern Pennines, south Lancashire and the Brecklands, but many smaller and very important pockets of semi-natural vegetation exist over the entire area where the critical level is exceeded. It should also be noted that important pockets of semi-natural vegetation, of high local amenity and conservation value, also occur within urban areas.

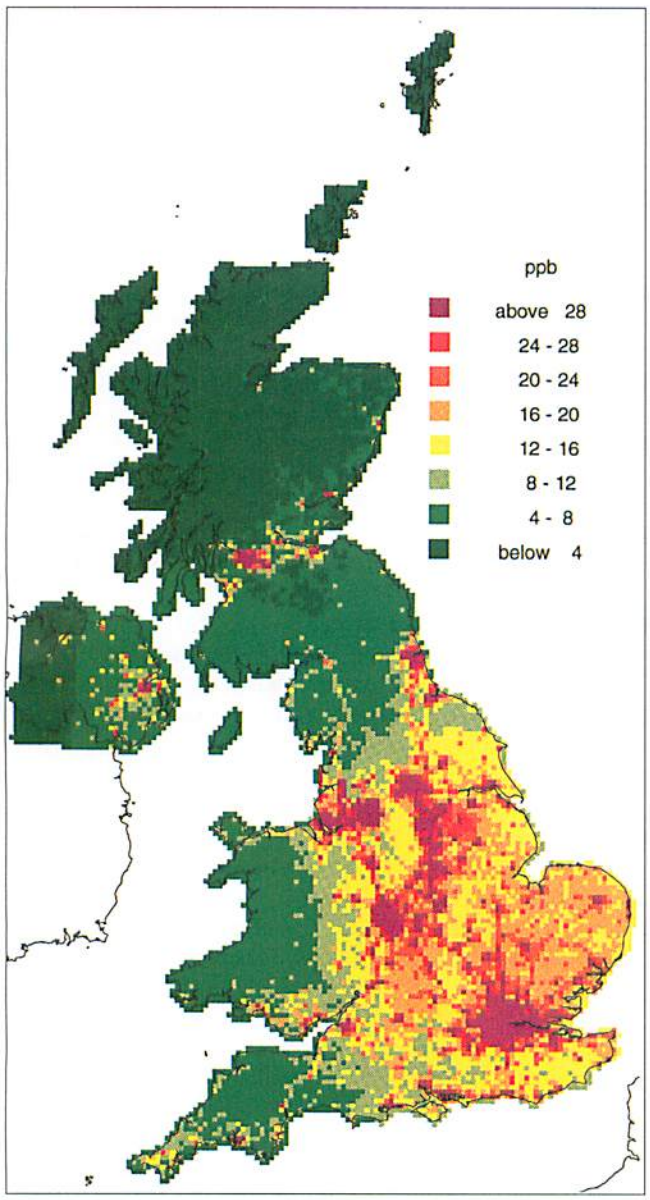

Figure 6.14 Estimated annual mean NO_x (ppb) for 1994 (from rural NO_2, land cover and roads data), Stedman at AEA Technology (NETCEN).

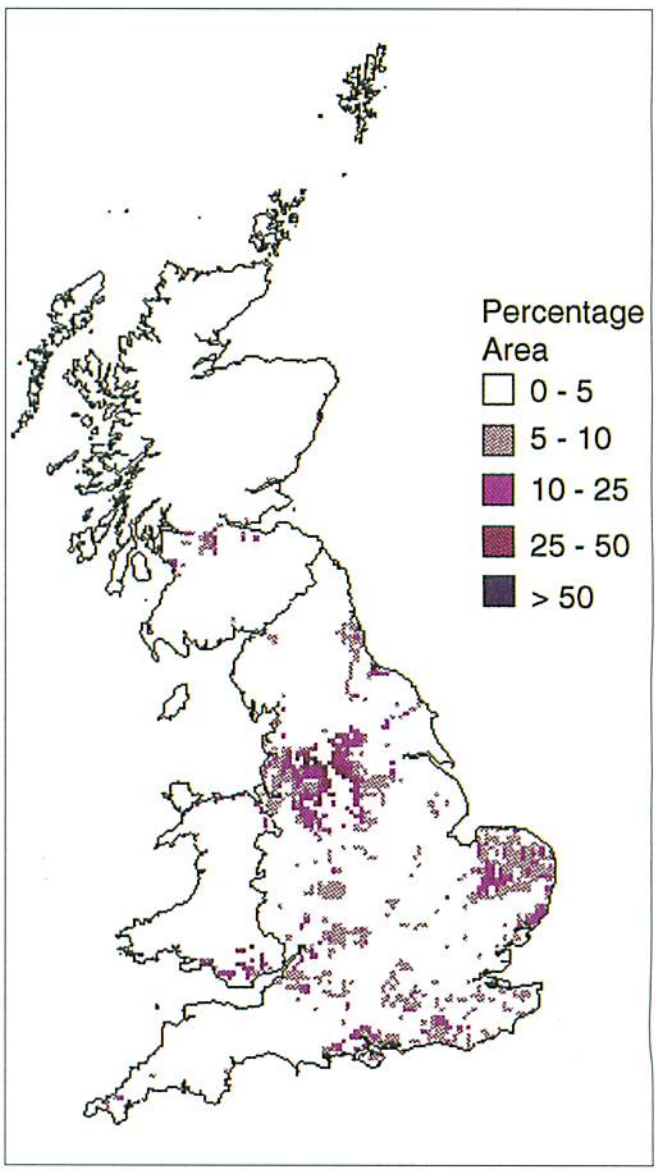

Figure 6.15 Percentage areas of semi-natural vegetation where the urban corrected annual mean NO_x for 1994 exceed the critical level. Supplied by the Environmental Information Centre, ITE.

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7. EFFECTS OF OZONE ON VEGETATION, MATERIALS AND HUMAN HEALTH

1 Vegetation

- The assessment of environmental risk related to ozone effects on vegetation is currently based around the critical level concept. Critical levels are defined using the AOT40 index - the cumulative exposure over 40 ppb during a growing season.
- At an international workshop in Kuopio, Finland in April 1996, revised critical levels of ozone were agreed to prevent damage to the most sensitive crops, forests, and natural vegetation.
- Using the assessment method and critical level values recommended at this workshop, the critical level for forests, an AOT40 of 10000 ppb h over six months, is only exceeded in southern Britain. The area in exceedance of the critical level represents 15% of UK land area, and 23% of UK forest area. In contrast, the critical level for crops and for semi-natural vegetation, an AOT40 of 3000 ppb h over 3 months, is exceeded almost throughout England and Wales, and in many parts of Scotland. The area in exceedance of the critical level represents 81% of UK land area, 91% of UK area of arable crops, and 76% of UK area of semi-natural vegetation. There is limited experimental evidence of impacts on vegetation in certain of the areas where the critical level is exceeded.
- Exceedance of the critical level does not mean that there will be damage to vegetation, but only that the risk of damage exists for sensitive species and conditions. Furthermore, the degree of exceedance of the critical level cannot be used directly to estimate the extent of damage to vegetation, or to assess the economic impacts of ozone on vegetation.
- This is because exposure to high levels of ozone is correlated with high temperatures and irradiances, and high vapour pressure deficits. For example, there is considerable variation between years in the AOT40 values found in the UK, but the years with high values of AOT40, and wider exceedance of the critical level, are often the hotter and drier years in which accumulated soil moisture deficit is greater, and hence ozone uptake by vegetation is lower.
- AOT40 values are calculated over a fixed three or six month growing period, but this may not reflect actual UK growth periods. Furthermore, the ozone sensitivity of vegetation is not constant, but varies with the stage of plant development. The timing of ozone episodes varies between years and sites in the UK, and this will significantly alter the impact on vegetation.
- Analysis of the seasonal patterns of AOT40 across the UK shows large variations from year to year. Data averaged over several years showed a more consistent pattern:- in April and May, there was relatively little difference in AOT40 values across the UK, but for the rest of the summer months, there was a large gradient from southern sites, where large additional AOT40 exposures occurred, to remote northern or western sites, at which almost no additional AOT40 exposure occurred.
- Recent UK and Scandinavian studies have shown large gradients in AOT40 values between the standard measurement height of the monitoring network, and the height of the vegetation, in the case of crops and semi-natural vegetation. This means that exceedance of the critical level estimated using the national network may significantly overestimate the true area of exceedance in the UK.
- There is an urgent need to estimate more accurately the real impact of ozone on vegetation in areas of the UK where the critical level is exceeded. This will require further experimental and modelling work, so that the effect of factors such as variation in sensitivity between species, the effects of climatic and edaphic factors, and the timing of ozone episodes, can be quantified. A key focus of this work will be the development of methods to map the uptake of ozone by vegetation, and to quantify the relationship between this uptake and observed effects.
- Within the UK vegetation effects assessment it has not been possible to modify the maps of AOT40 for the urban reduction in exceedance.

2 Materials

- Ozone has a damaging effect on certain materials, including polymers, rubbers, surface coatings and textiles.
- Material damage is related to the annual mean ozone concentration, which is lowest in urban areas where the density of at-risk materials is highest.
- A preliminary critical level for material damage was set at 20 ppb as an annual average concentration, at a UNECE workshop in 1993. This level is currently exceeded in most of the UK with the exception of some urban areas.
- As measures to control the emissions of VOCs and NO_x come into effect, ozone levels may rise in urban areas with an associated increase in the cost of damage to materials.
- Estimates of the current cost of damage range from £100 to £345 million for the UK. However the methods used to produce these estimates are very uncertain and can only give an indication that the costs are substantial.

3 Human Health

- Ozone is the most irritant of the common air pollutants and exposure to concentrations commonly encountered in the UK has been shown to produce inflammation of the respiratory tract.

- In terms of effects on standard physiological indices of lung function there is no evidence to suggest that asthmatic subjects are more sensitive to ozone than other individuals. However there is evidence based on studies of the inflammatory response to the airways induced by exposure to ozone to suggest that asthmatic subjects are a little more sensitive than others.
- The combination of ozone and acid aerosols may have a more marked effect than exposure to ozone alone.
- Long term exposure to ozone in the USA at average concentrations greater than those encountered in the UK has been shown to be associated with a chronic decline in lung function.
- A recent study has demonstrated that ozone levels in London are associated with changes in daily mortality rates. Cardiovascular and respiratory mortality were affected with the effects being most marked during the summer season.
- Recent time-series studies of the effects of daily variations in concentrations of ozone and indices of ill-health including hospital admissions and mortality have shown that there may be a threshold of effect at about 40-60 ppb ozone, 8 hour average concentration.
- Depending on the assumptions made about thresholds of effect for ozone, a wide range of hospital admissions related to ozone could be derived. These range from 0.35% to 6.1% of total admissions for respiratory disorders. The Department of Health Committee on the Medical Effects of Air Pollutants will investigate this further and report later in 1997.
- Because admission to hospital for respiratory disease is a relatively rare event, the effect of ozone on hospital admissions, already small in relative terms, is likely to have only a small public health impact. However, panel studies indicate that ozone also increases the risk of a worsening of symptoms or increased medication requirement. Although this is a small relative effect, a large number of people are at risk and when the widespread exposure to ozone is also taken into account, the health impact of increased ozone levels is likely to be greater than the effect on hospital admissions suggests.
- New evidence from the UK and from elsewhere confirms the conclusions of the Department of Health Committee on the Medical Effects of Air Pollutants that, at the population level, air pollution has a detectable but relatively small effect on the provocation of existing asthma, and is unlikely to play a role in the incidence of new asthma.

7.1 The Effects of Ozone on Vegetation

Over the past 20 years, a substantial body of evidence has accumulated to demonstrate that current concentrations of ozone in many parts of Europe, including the UK, may have adverse effects on crop yield, tree growth and vitality and the composition of natural communities. Earlier reports of the review group (PORG, 1987, 1993) have assessed the evidence of impacts on vegetation in the UK, and in the last report (PORG, 1993) the concept of a critical level for ozone was introduced.

A critical level of an air pollutant is defined as "the concentration of a pollutant in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials, may occur according to current knowledge" (UNECE, 1988). The aim of preventing or minimising the effects of ozone on vegetation will be an important consideration in the negotiations within the United Nations Economic Commission for Europe (UNECE) of new VOC and NO_x Protocols over the next few years. Within these negotiations, the critical level approach will be the key element in translating our understanding of impacts of ozone on vegetation into policy objectives. It is hence of considerable practical significance not only that the actual values of critical levels should be defined as precisely as possible by the scientific community, but that these values should be used properly in the assessment process. Furthermore, it is important that the uncertainties in both setting and mapping critical levels are properly assessed, as these may be important in policy evaluation. There is, however, an inevitable tension between the biological complexity of responses to ozone and the need for a critical level approach which can be readily incorporated in policy assessments.

7.1.1 Defining Critical Levels

Critical levels for ozone were first proposed at a workshop at Bad Harzburg in 1988 (UNECE, 1988). However, radical changes to this critical level approach were proposed at the 1992 Egham workshop (Ashmore & Wilson, 1994), and at the subsequent 1993 Bern workshop (Fuhrer & Achermann, 1994) new critical levels were formally adopted. Finally, at the Kuopio workshop in April 1996, the critical levels established in Bern were re-examined, and a new set of values adopted for use within UNECE (Karenlampi & Skarby, 1996). The development of the critical level concept for ozone at these successive workshops is described in more detail in Sections 7.1.2.1 and 7.1.2.2 below.

The experimental basis for the critical levels set at the Bern and Kuopio workshops has been reviewed in the recent report of the CLAG Vegetation Effects Subgroup (CLAG,1996) in the UK context. That report also considered uncertainties in the derivation of these critical levels, and made a number of recommendations for improving the scientific basis for applying these critical levels in the UK. It also presented maps of critical levels and their exceedance in the UK, produced following precisely the recommendations of the Kuopio workshop. The reader should consult CLAG (1996) for a more detailed discussion both of ozone impacts and of the current scientific basis of the critical levels for ozone. In Section 7.1.2 of this chapter, the current critical levels are described and the key uncertainties in setting the values are briefly considered.

However, the primary purpose of this chapter is to examine critically a series of issues which arise when actually applying the ozone critical levels adopted at

the Bern and Kuopio workshops to develop an effects-based international or national control strategy aimed at reducing the impacts on vegetation of ozone and associated air pollutants. Such a policy would require, among other elements:-

(a) a definition of the appropriate critical levels.

(b) maps showing geographically resolved critical levels, assigned on the basis of the presence of appropriate receptors, or vegetation types.

(c) maps showing geographically resolved current ozone exposures.

(d) maps showing the geographical variation in exceedance of the critical level, based on an overlay of (b) and (c).

(e) maps showing modelled ozone exposures based on current or future emission scenarios.

(f) maps showing predicted future exceedance of ozone critical levels, based on an overlay of (b) and (e).

It is clear that for this process to work effectively, and for the scientific basis of control policy to be soundly based, it is essential that there is consistency in the approaches taken at each of these steps. This requires a truly interdisciplinary approach to the problem, with dialogue between members of the effects, measurement, mapping, modelling and policy-making communities to ensure that key issues, in particular in relation to the spatial and temporal scale of the intercomparisons, are identified and resolved. Since the PORG group contains just such a mix of expertise, this aspect of the assessment of impacts on vegetation through the critical levels approach will be considered in Section 7.1.4 of this chapter.

7.1.2 Development of Critical Levels

7.1.2.1 The Cumulative Approach

The importance of ozone effects on vegetation was first recognised in the US, and when the critical levels for ozone were first set, at the Bad Harzburg workshop in 1988, the experimental data used were largely drawn from American studies. Three critical levels for ozone were adopted on the basis of this workshop, based on three averaging times:-

- 1 hour (75 ppb)
- 8 hours (30 ppb)
- 'growing season' (25 ppb as a seasonal 7-h mean)

The 7 hour (0900-1600) mean was originally selected as the basis of the long-term critical level because it was the parameter originally used in the study which provided the best scientific basis for setting this value. This was the National Crop Loss Assessment Network (NCLAN), a research programme involving exposure-response studies at several locations in the US (Heck *et al*, 1988). The 7 hour mean concentration was used in the last PORG report to provide a preliminary quantitative assessment of the impacts of ozone on agriculture in the UK.

However, in the USA, concerns about the value of the 7 hour mean concentration as the basis for vegetation effects analysis has led in recent years to attempts to assess different ozone exposure indices. A number of American studies have compared ozone exposure indices which give greater weight to higher concentrations with those based on means, in which all concentrations implicitly have the same weight. A number of mathematical methods have been used to weight concentrations, e.g. by simply accumulating hours above a threshold or cut-off concentration, or by applying a range of sigmoid functions. The approach of weighting hourly ozone concentration records has been extended further, for example by applying a phenological weight to take account of changes in plant sensitivity through the growing season.

Several such studies have attempted to assess the performance of different indices using data for a range of crops from the NCLAN programme. For example, Lee *et al* (1988) used data for soybean, wheat, corn, sorghum and cotton for different sites and years to test as many as 613 different ozone indices. The study clearly demonstrated that indices which emphasised peak concentrations or accumulated exceedances of a threshold gave a better fit to yield data than did mean concentrations. Similar conclusions have been reached by Finnan *et al* (1995), based on analysis of European data.

There are also further difficulties associated specifically with the 7 hour averaging time of 0900 to 1600. This period was originally selected for the NCLAN study as corresponding to the period of greatest plant sensitivity, and the highest level of ozone. However, in many rural areas of Europe, peaks occur much later than this, and last for longer than 7 hours.

In devising an appropriate ozone exposure index, it is important to distinguish between two distinct applications. Firstly, there is the question of assessing which index provides the best fit to a range of experimental data on plant response. In this case, elaborate exposure indices which provide different weightings for exposures at different phenological stages, for different concentrations or for different times of day, may be quite appropriate, and the process of evaluation of different ozone exposure indices may provide valuable insights into mechanisms of ozone impacts on vegetation.

However, while such indices may provide the best fit to experimental data, they are complex, and often specific to particular data sets. They are thus inappropriate for the second application, which is to devise an index which is appropriate for use in formulating a critical level, or an air quality standard, which is to be used in the assessment of pollution control policy. Such an index must, of course, provide a measure which is meaningful in terms of plant response, but it must also be robust, easily mapped and also readily produced as an output of regional models used to predict the effects of different control strategies on ozone distribution and concentrations on a European scale (Ashmore, 1994).

For these reasons given above, the main conclusion of the Egham workshop, in March 1992, with respect to ozone was that the concept of a cumulative exposure above a fixed concentration threshold should be adopted for the long-term critical level in place of the existing 7-hour mean concentration (Ashmore & Wilson,

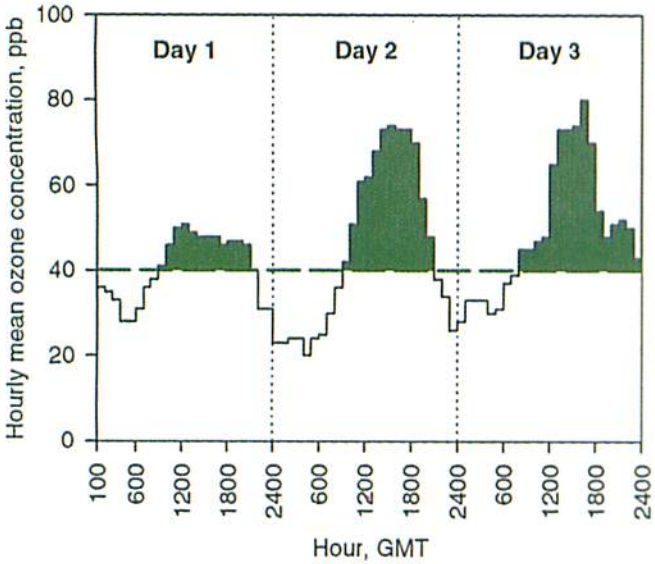


Figure 7.1 Example of 3-day time course of hourly mean ozone concentrations (Eskdalemuir, 22-24th May 1995). Hourly concentrations above a cut-off concentration (shaded area) are summed over the exposure period of interest to calculate the cumulative exposure index. In this example, 40 ppb is chosen for the cut-off concentration (from original example in Fuhrer *et al*, 1995).

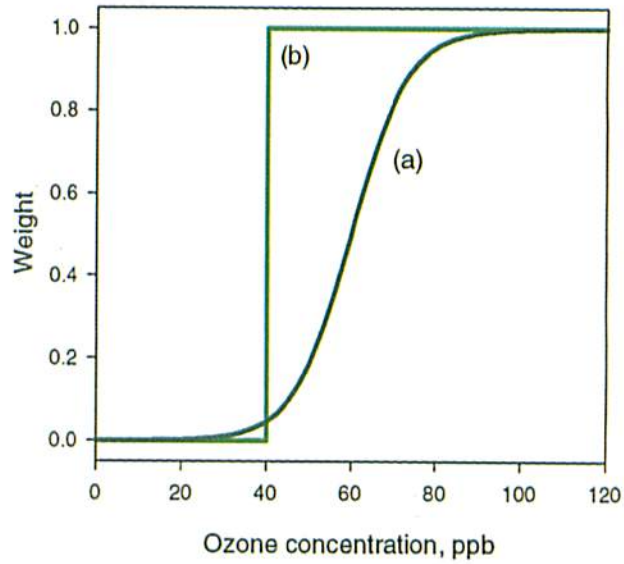


Figure 7.2 Illustration of ozone concentration weighting using (a) continuous weighting with a sigmoidal function which gives increasing weight to increasing concentrations, or (b) discontinuous weighting with a cut-off concentration which gives equal weighting to all concentrations above the cut-off concentration (from original example in Fuhrer *et al*, 1995).

1994). It was recommended that the cumulative exposure should be calculated for daylight hours only over the growing season of the particular receptor. This approach is illustrated using typical diurnal patterns of ozone exposure in Figure 7.1. When the concentrations of ozone are below the threshold concentration, the exposure is zero, while when they exceed the threshold the difference between the actual and threshold concentrations is added to the cumulative exposure.

It should be emphasised that in setting a threshold concentration, it is not intended to indicate that concentrations below that threshold have no biological effect. Instead, the cumulative exposure above a threshold can be seen as a square-wave simplification of a sigmoidal exposure-response function (Figure 7.2), i.e. that concentrations below the threshold are given no weight, while those above are given maximum weight. To avoid confusion, it is preferable to refer to a cut-off concentration rather than a threshold concentration.

7.1.2.2 Current Critical Levels

The UNECE workshop on critical levels for ozone which took place in Bern in November 1993 (Fuhrer & Achermann, 1994) had the main objectives of determining whether the concept of defining a critical level based on cumulative exposure above a cut-off concentration, as proposed at Egham, was a valid approach for European crops and trees, and defining the appropriate cut-off concentration and cumulative exposure values for the critical level. These values were critically examined in the context of further scientific analysis at the subsequent workshop at Kuopio, in April 1996 and a revised set of critical levels adopted (Karenlampi & Skarby, 1996). The following sections briefly review, for the three major types of vegetation, the scientific basis of the critical levels adopted at the Bern workshop and the reasons for the revisions made at the Kuopio workshop.

Agricultural crops

Discussions at the Bern Workshop focused on the recently released results of a major international programme of research into the effects of ozone pollution on crops (Jager *et al*, 1994). This programme, named the European open-top chamber experiment (EOTC), was conducted in 9 countries over 5 years from 1987-1991. The experiments involved the exposure of crops to a range of ozone concentrations in open-top chambers over most of their growing season. In this way, exposure-response relationships for parameters such as reductions in yield quality or quantity, could be estimated. Several crops were studied in the programme, including wheat, barley, beans and pasture.

Analysis confirmed that yield reduction was highly correlated with the cumulative exposure above a threshold of either 30 or 40 ppb (Fuhrer, 1994). The use of a threshold of 50 ppb clearly led to a worse fit to the experimental data. It was considered more appropriate to use 40 ppb as the threshold for the critical level because this concentration is just above the range of background ozone concentrations in Europe. The exposure index is referred to as the AOT40 (accumulated exposure over a threshold of 40 ppb). The parameter was to be calculated for daylight hours only because the uptake of ozone at night was considered to be negligible for crops due to closure of the stomata.

Wheat was selected for the derivation of the critical level because the data base was more comprehensive and because the crop appeared to be relatively sensitive to ozone. Indeed, the spring wheat data set included data for four cultivars, four countries, and five years of

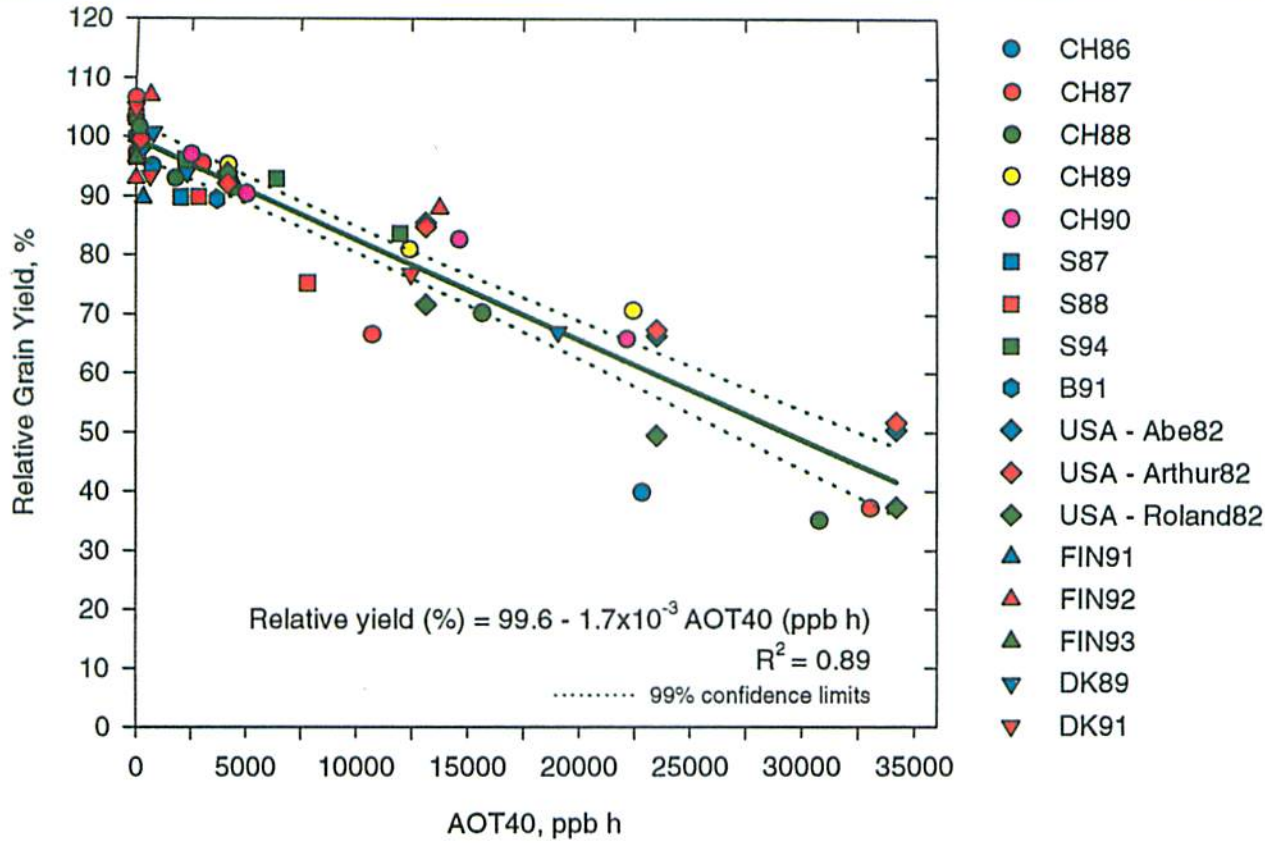


Figure 7.3 The relationship between relative grain yield of spring wheat and ozone exposure expressed as AOT40 over three months, based on data from several European and US open-top chamber experiments. From Fuhrer (1994).

experiments. Despite the variable data sources, a strong linear relationship between AOT40 and the relative yield of spring wheat was found (Figure 7.3). This relationship can be used to determine the yield loss in the experimental system associated with AOT40s up to 35000 ppb h. After considerable discussion, it was decided that the AOT40 associated with a 10% yield reduction would be the most appropriate value to use as the critical level for ozone. This figure is the minimum yield reduction which could have been established in a well designed experiment of the type and scale of the EOTC. Thus it represents the practical likelihood of being able to verify that reductions in crop yield do actually occur in areas where the critical level is exceeded. The critical level corresponding to the 10% yield reduction was 5300 ppb h. However, the fitted line in Figure 7.3 could be used to calculate critical level values corresponding to any yield reduction figure thought to be acceptable.

In defining a cumulative exposure index, it is important to consider the time-period over which it is to be applied. A time period of three months was suggested for the definition because this represented the average length of the EOTC wheat experiments. It is also the time period for which spring-sown crops are actively growing, and therefore are most likely to be sensitive to ozone. The months of May, June and July were recommended for use in northern and central Europe, as these months are the period of maximum growth, and are frequently the months with highest ozone concentrations. The year in the last five years for which the three month AOT40 was highest was recommended for mapping purposes, as the objective was to prevent a 10% yield loss in the worst ozone years.

For the Kuopio workshop, data from additional experiments were added to the relationship shown in Figure 7.3, including data from US experiments. These were consistent with the existing linear relationship to AOT40, but their inclusion altered the critical level corresponding to a 10% yield reduction to 5900 ppb h (Fuhrer, 1996). However, statistical analysis of the combined wheat yield dataset by Pleijel (1996) indicated that the least significant yield loss which could be detected with 99% certainty was 4-5%. A yield loss of 5% corresponds to a critical level of approximately 3000 ppb h. However, it was also decided that this should be compared with the mean annual AOT40 value, calculated over the most recent five years, as it was argued that whereas a yield loss of 5% in one year would have little economic significance, a yield loss of 5% every year would of significance to the farming community.

In summary, the critical level for agricultural crops which was established at the Bern Workshop was 5300 ppb h above 40 ppb ozone accumulated during daylight hours for the three months when the crop is most sensitive to ozone (May, June and July for northern Europe), to be compared with the AOT40 value in the worst year in five. This was altered at the Kuopio workshop to a value of 3000 ppb h, to be compared with the mean AOT40 value over the last five years. It is important to note that this change is based on a different interpretation of essentially the same exposure-response relationship.

A critical level for visible injury based on an evaluation of field observations of injury development in ambient air as part of the UN/ECE ICP-Crops programme was recommended at the Bern workshop (Sanders, 1994), and was modified at the Kuopio workshop based on further analysis (Benton *et al*, 1996). However, it has not proved possible to map exceedance of this critical level effectively in the UK, although it is clear that it is exceeded at least once in most years in many areas of the UK (CLAG, 1996).

There are a number of uncertainties associated with the critical level for yield reduction in crops. Firstly, the value was derived from open-top chamber experiments in which the flux of ozone into the plants may have been overestimated. Secondly, the definition is based on spring wheat, a crop which is currently grown on less than 1% of the cereal growing area in the UK. Further experiments are necessary to determine the relative sensitivity of spring wheat compared to other crops such as sugar beet and potato for which there is little or no current information and to confirm that the same relationship is appropriate for winter wheat. Thirdly, there is evidence that ozone episodes may have greater impacts at critical growth stages, such as grain fill (Pleijel *et al*, 1996), and this is overlooked in the definition. Finally, the current definition assumes that the crops are well watered, and that climate has no impact on the critical level.

Forest trees

Determining a critical level for forest trees is a difficult task, compared to annual crops. Long-term experimental data on the responses of mature forest trees are practically non-existent and therefore analysis is primarily based on studies using seedlings or juvenile trees. Apart from the obvious problem of scaling up from seedlings to mature trees, their perennial nature and longevity has also to be considered. In addition, analysis of experimental data for the same species shows much greater variability both within and between experiments than is the case for crops.

For these reasons, and because at the time relatively few peer-reviewed studies meeting the selection criteria were available, the critical level proposed at the Bern workshop was provisional in nature. By the time of the Kuopio workshop, more data were available allowing exposure-response relationships using the AOT40 index to be derived for two species, Norway spruce and beech (Skarby and Karlsson, 1996). Of these two species, it was clear that beech was more sensitive to ozone, and thus this was selected for determination of the critical level. Two major criteria were used to select suitable data for this species:- (i) that the experiment was carried out under conditions close to those in the field (e.g. in open-top chambers) and (ii) that a range of environmentally realistic ozone exposures were used.

A number of different responses could be used as the basis for determining the critical level, given that ozone exposure can cause many subtle physiological responses, which may lead to altered sensitivity to other major environmental stresses, such as frost and drought. Such stresses can cause long-term changes in forest vitality; for example, the drought of 1975/1976 reduced beech growth at many sites in southern Britain over a period of 5-10 years. However, it was agreed that a more robust criterion, the annual biomass increment, was needed, because it is a relevant integrated response parameter of direct economic relevance.

The data for young beech trees used originated primarily from studies in Switzerland (Braun & Fluckiger, 1995). In these experiments, the minimum detectable effect at 95% confidence was a biomass decrease of 10% (Figure 7.4). The critical value of AOT40 of 10000 ppb h provisionally agreed at the Bern workshop was estimated to be within the range of AOT40 values, corresponding to a 10% biomass decrease, taking into account the uncertainty in the fitted relationship; thus this value for the critical level was retained.

Some changes were made to the basis on which the critical level is calculated, although its value, and the time of year over which it is calculated (a 6 month growing season starting on 1 April), remained the same. Firstly, as for crops, the AOT40 values for comparison with the critical level should now be calculated as the 5 year mean AOT40, rather than that for the worst year in the last five. This is consistent with the long-term nature of ozone impacts on forest trees. A further change related to the period of the day over which the AOT40 value for comparison with the critical level is calculated. At the Bern workshop, it was agreed that, unlike the critical level for crops, that for forest trees should be calculated over all 24 hours. This was because of some experimental evidence of limited ozone uptake at night in spruce and larch (Weiser & Havranek, 1993; 1995). However, these measurements were made in stirred branch chambers, and most evidence from micrometeorological studies suggests that ozone deposition to forest canopies is minimal at night (e.g. Coe *et al*, 1995). Thus at the Kuopio workshop, it was recommended that the AOT40 for comparison with the critical level for trees should be calculated for daylight hours only.

In summary, the critical level for forest trees is now an AOT40 value of 10000 ppb-h. For comparison with the critical level, values are calculated for daylight hours over a 6 months growing season, based on a 5 year mean.

Although the experimental evidence for this critical level is now a little stronger than when it was first proposed at the Bern workshop, it should be emphasised that it is still based on very limited data and a number of large assumptions about the responses of trees to ozone over time-scales of decades. A considerable amount of research is required in the future to assess the validity of the proposed critical level and to determine whether the critical level is acceptable for a wider range of European forest trees, including southern European species.

Semi-natural vegetation

The most important impact of ozone on plant communities may not be through an impact on growth or productivity, or through visible injury, but through shifts in species composition, loss of biodiversity,

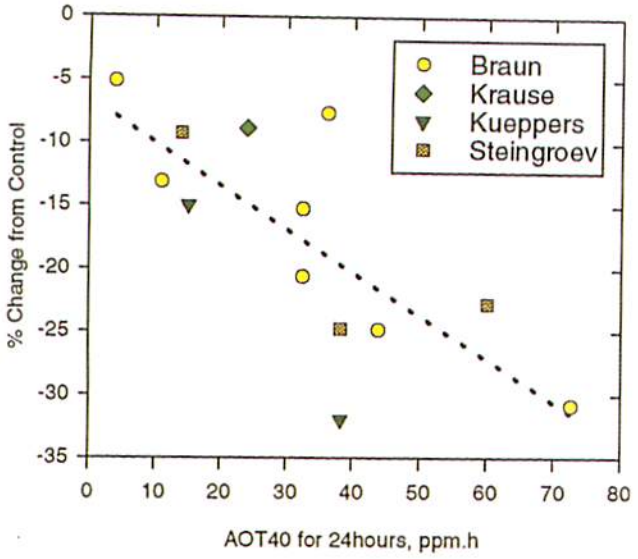


Figure 7.4 Exposure-response relationship, based on the AOT40 index, for biomass production of Norway spruce and beech. From Skarby & Karlsson (1996).

and changes in genetic composition. No critical levels were set at the Bern workshop for semi-natural vegetation, primarily because of the paucity of experimental data, but more data were available for discussion at the Kuopio workshop.

There are very few European experiments which provide exposure-response data for ozone effects on semi-natural vegetation. The most useful European exposure-response data comes from open-top chamber studies of real or artificial grassland communities. Studies in Switzerland (Fuhrer *et al*, 1994) and in the UK (Ashmore & Ainsworth, 1995) do provide evidence of significant shifts in species composition in such communities in response to ozone. Although the data (Figure 7.5) show more scatter than do similar plots for crop yield, they provide strong evidence of a linear response to ozone exposure expressed as AOT40. It is clear from these, and other, studies that effects on the relative proportion of different species are observed at much lower ozone exposures than effects on total biomass or productivity. Both studies involved grass/forb mixtures, with the forb component, which in both cases included clovers, decreasing with increasing ozone exposure.

As in the case of crops, it is possible to calculate from the exposure-response relationship the ozone exposure corresponding to a given effect. Selecting a reduction of 10% in the proportion by biomass of the sensitive species as the criterion, the equivalent ozone exposure was 6.3 ppm h for the Swiss data, and 5.7 ppm h for the UK data on cut swards; subsequent unpublished UK experiments using different species mixtures have given values of 7-8 ppm.h. There is also evidence from field studies in the UK that the ozone resistance of plantain populations is correlated with the ozone concentrations where they were collected (Reiling & Davison, 1992). This suggests that ozone is having sufficient adverse effects on the more sensitive genotypes within the population to give the less sensitive genotypes a competitive advantage. AOT40 values

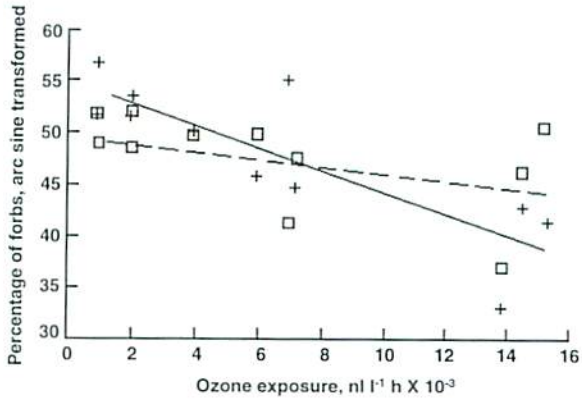


Figure 7.5 Exposure-response relationships, based on the AOT40 index, for percentage of forbs in artificial acid grassland swards which were cut (solid line) or uncut (dotted line). From Ashmore & Ainsworth (1995).

correlated well with ozone tolerance, and it was calculated that a change in tolerance of 5% (the minimum which can be detected experimentally) corresponded to an AOT40 value of about 5000 ppb h (CLAG, 1996).

This evidence from field experiments and observations is now supported by controlled fumigation studies of individual plants (Ashmore & Davison, 1996). These studies clearly suggest that the most sensitive species of semi-natural communities are as sensitive to ozone as the most sensitive crop species. Recent work by Bergmann *et al* (1996) has shown large significant effects on vegetative and reproductive parameters of several such species in response to AOT40 exposures of about 4000 ppb h.

In the light of this information, it was agreed at the Kuopio workshop that, although the experimental data relating to species of semi-natural communities were still too limited to be used to estimate critical levels directly with adequate certainty, it was reasonable to assume that such species could be at least as sensitive as arable crops, and thus that the critical level for crops (3000 ppb h during daylight hours over a 3 month growing season) should also be applied to semi-natural vegetation.

Indeed, in view of the very high sensitivity to ozone of some individual species of such communities, there may be a need to lower the critical level further. However, this would require a much larger and more consistent set of experimental data than currently exists.

Level I and Level II approaches

The Bern and Kuopio workshops essentially adopted a Level I approach to setting a critical level. In this approach, a single value is assigned to all crops, all tree species, or all semi-natural vegetation, under all environmental conditions. This is essentially a precautionary approach, in which critical levels values are set based on the response of the most sensitive species under the most sensitive environmental conditions for which strong and consistent scientific data exist.

However, it is well-known that large innate variations in response to ozone exist between species (and indeed between cultivars and ecotypes), and that environmental conditions significantly alter plant responses. This means:-

(a) that the fact that the critical level is exceeded in a particular location does not mean that there will be adverse effects on the vegetation at that location; it only indicates the potential risk of such damage.

(b) that exceedance of the critical level is not directly related to the actual degree of damage to vegetation.

This second point appears to contradict the existence of linear relationships between AOT40 and yield loss, or other response variables, such as that in Figure 7.3. However, these relationships have been derived in open-chamber experiments in which the same cultivar is exposed to a range of ozone exposures under identical edaphic and climatic conditions and with identical atmospheric turbulence. In contrast, when comparing AOT40 values in different regions, or in different years, soil moisture conditions, vapour pressure deficit, atmospheric conductivity and many other factors known to affect vegetation responses to ozone, may well also differ. In addition, different species or cultivars may be grown at these different locations, and the timing of ozone episodes may differ.

The so-called Level II approach to critical levels would attempt to incorporate these factors to produce a more accurate and detailed assessment of real ozone impacts. However, the implementation of a Level II approach for ozone is currently not feasible because of the very limited body of direct scientific evidence on which to define this variation in sensitivity. Moreover, implementation of such a Level II approach on a European scale would place considerable demands on available maps and data-bases, and its application is certainly constrained by current mapping data availability (Ashmore & Emberson, 1996). However, work is underway to develop such a Level II approach, for example by incorporating the effects of soil moisture deficit on responses to ozone (Fuhrer, 1995; Emberson *et al*, 1996; Brown *et al*, 1996a).

Comparison of European and US Approaches

In the United States, there have also been extensive discussions in recent years of the choice of an appropriate exposure index which can be used to quantify exposure-response relationships and to asses the geographical variation in the risk of ozone impacts. The conclusion reached is broadly consistent with those of the European analysis of exposure-response relationships in that indices which emphasised higher concentrations and which incorporated the duration of exposure provided the best fit to experimental data (Lee *et al*, 1988; Musselman *et al*, 1994). As in Europe, the simple exposure indices selected for risk analysis have been criticised as simplifying the dynamics of plant responses to ozone, or not taking into account key environmental variables which influence the flux of ozone to vegetation in the field, as opposed to chamber conditions (e.g. Krupa *et al*, 1994).

The index adopted most widely in recent in the US for risk assessment (e.g. Hogsett et. al, 1997) is termed SUM60. This index has two key differences from the AOT40 index adopted in Europe. Firstly, the cut-off concentration is 60 ppb, rather than 40 ppb. Secondly, when the measured concentration exceeds the threshold, or cut-off, concentration, the whole concentration is added to the cumulative exposure index. Thus, a single hour's concentration of 70 ppb would contribute 30 ppb h (70 -40 ppb) to the AOT40, but 70 ppb h to the SUM60. Thus, the US index uses a higher threshold, but accumulates exposures more rapidly once the threshold is reached.

7.1.3 Critical Level Exceedance in the UK

7.1.3.1 Evaluation Based on Kuopio Workshop

Figures 7.6 to 7.8 show the evaluation of critical level exceedance for the UK, based on the recommendations of the Kuopio workshop. The three figures show:- (a) the distribution of AOT40 over the country, calculated as described above for the relevant vegetation types, (b) the distribution of the relevant vegetation type, and finally (c) an overlay showing where the critical level is exceeded and the vegetation type is present at high density.

It should be emphasised that, although these maps provide a simple risk assessment for ozone impacts on vegetation, the critical level approach is a precautionary one. Thus, exceedance of the critical level in a particular location does not mean that adverse effects will occur, only that a risk of damage exists for sensitive species and situations. It is also important to recognise, as emphasised above, that exceedance of the critical level is not proportional to the degree of yield loss, or any other biological response.

Figure 7.6 (a) shows that, for crops, the critical level is exceeded over most of Great Britain, with the exception of parts of Western Scotland, Cumbria, Lancashire, Anglesey and the East Midlands. The total land area of the UK in exceedance of the critical level is 81%.

Figure 7.6 (b) shows the percentage land cover of arable crops over the UK, while Figure 7.6(c) shows this only in the areas of exceedance; it is those areas with high cover of arable crops which are in exceedance of the critical level, such as most of the English Midlands East Anglia and Eastern Scotland, which are of greatest concern; in contrast the areas of exceedance in much of Wales and in northern Scotland are of little concern in terms of impacts on agriculture. The total land area covered by arable crops in the UK which experiences exceedance of the critical level is 91%, indicating that most arable agriculture is at risk of adverse impacts of ozone. The precise areas in which the critical level is not exceeded will also be of particular importance in the East Midlands and in south Lancashire, given the significance of cereals and intensive horticulture in these regions. However, given the limited monitoring network available from which to produce these maps, it should be recognised that

there is considerable uncertainty over the precise location of the 3000 ppb h boundary (see Chapter 3).

For semi-natural vegetation (Figure 7.7), the critical level is the same as that for crops, and thus the area of exceedance is identical. The total land area covered by semi-natural vegetation in the UK which experiences exceedance of the critical level is 76%, a similar figure to that for arable crops. However, the distribution of this type of vegetation is very different, with the large areas in exceedance of the critical level with high percentage cover of semi-natural vegetation being found in Scotland, and the uplands of northern England, Wales, and south-west England.

In the case of forests (Figure 7.8), the area of exceedance of the critical level is much lower, representing only 15% of the UK land area, although this represents 23% of the UK forest area. This is concentrated in the south of England and south-east Wales, and Figure 7.8 (c) highlights areas such as the Forest of Dean and the New Forest as being potentially impacted by ozone. Beech woodlands in areas such as the Chilterns and Cotswolds also may be of particular concern in view of the beech being identified as an ozone sensitive species and data from this species being used to define the critical level.

7.1.3.2 Validation of Critical Level Exceedance

In view of the number of uncertainties involved in defining critical levels of ozone and mapping areas of exceedance of the critical level, it is of considerable interest to ask whether there is any evidence of adverse impacts of ozone on vegetation in areas of exceedance. Such evidence would come from experiments in which ambient air was filtered to remove pollutants in locations where ozone is the dominant air pollutant.

In the case of crops, extensive filtration experiments at Ascot, west of London. have provided clear evidence of visible injury and reductions in growth and yield of sensitive crops, which are associated with periods of high exposure to ozone (Ashmore *et al*, 1980; Ashmore 1984). For forest trees, the most extensive filtration experiments are those of the Forestry Commission, who used three sites, in Hampshire, in the Pennines and in Perthshire. Significant reductions in the growth of beech and Scots pine occurred in ambient air at the Hampshire site, but not at the two more northern sites (UK TERG, 1993), which is entirely consistent with the map of critical level exceedance in Figure 7.8.

Finally, in terms of semi-natural vegetation, effects of filtration on grassland community composition have been reported at the Ascot site (Evans & Ashmore, 1992). The work of Reiling & Davison (1992), showing that southern populations of plantain are more ozone-tolerant, is also consistent with critical levels for semi-natural vegetation being exceeded over most of the country, although interpretation of field observations is always more problematical than that of experimental studies. More recent work by Reiling & Davison (1995), which shows year-to-year variation in plantain ozone tolerance which is associated with ozone exposures in the previous summer, is consistent with ozone being the causal factor.

In summary, the limited evidence available is not inconsistent with the critical levels exceedance maps shown in Figures 7.6 to 7.8. However, only a limited number of studies directly relevant to validation have been completed.

7.1.3.3 Comparison of Exceedance Mapping Using the Bern and Kuopio Guidelines

As explained in Section 7.1.2, there have been a number of significant changes both in the values of the critical levels, and in the methods used to calculate them and to map exceedance, between the Bern and Kuopio workshops. It is therefore of interest to compare the exceedance patterns for the UK produced using the recommendations from the two workshops. This is shown for crops in Figure 7.9, and for forests in Figure 7.10; since no critical level for semi-natural vegetation was adopted at the Bern workshop, this comparison is not relevant.

In the case of crops (Figure 7.9), the effect of the changes adopted at the Kuopio workshop is to substantially increase the area of the UK in exceedance of the critical level. Substantial areas of Scotland and of northern England are now shown to be in exceedance of the critical level. In terms of the percentage of total UK land area, there has been an increase in the exceedance area from 25% to 81%, and in terms of arable crop area, there has been an increase from 29% to 91%.

In contrast, the effect of the changes adopted at the Kuopio workshop for forest trees (Figure 7.10) is to reduce the area of the UK in exceedance of the critical level, with forest areas in small areas on northern England and Scotland, and much of Wales, no longer experiencing exceedance of the critical level. In terms of total area of the UK, there has been a decrease in the exceedance area from 30% to 15%, and in terms of forest area, a decrease from 40% to 23%.

Thus there are substantial differences between the maps of exceedance produced using the recommendations of the two workshops. This is largely because the UK's position in Europe is close to the limits of the area in exceedance of the critical level and thus it is sensitive to relatively small changes in the values of critical levels. In contrast, in many countries of central Europe, all areas would experience AOT40 values well above the critical level using either the Bern or the Kuopio approaches.

The changes between the two workshops, furthermore, reflect the current uncertainties in the formulation of critical level methodologies and values, and the limitations of current scientific understanding of ozone impacts, especially on forests and semi-natural vegetation. These uncertainties and limitations clearly have significant implications for the assessment of critical level exceedance, and hence the evaluation of the need for control measures, in the UK.

It is thus important to understand more fully each of the uncertainties in setting and mapping critical levels,and their implications for the UK. In addition, there are a number of other uncertainties in the mapping and assessment process. Finally, as stated previously,

A.

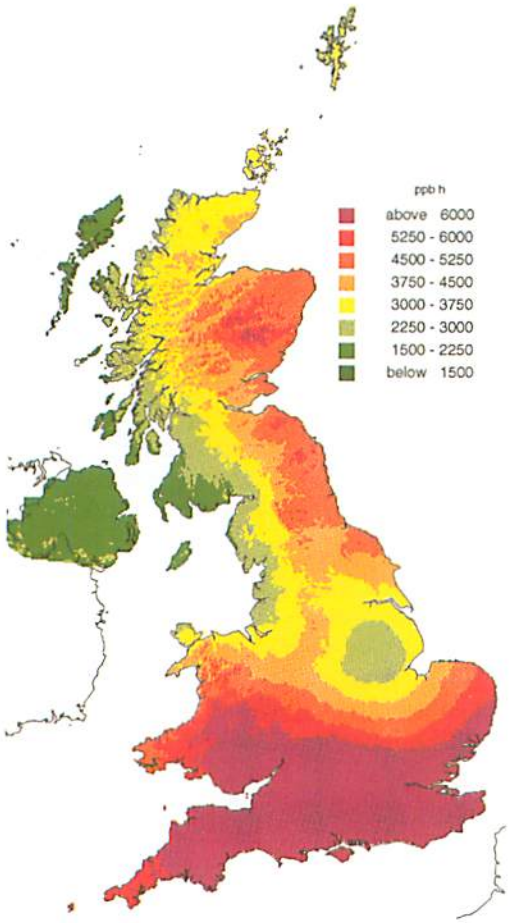


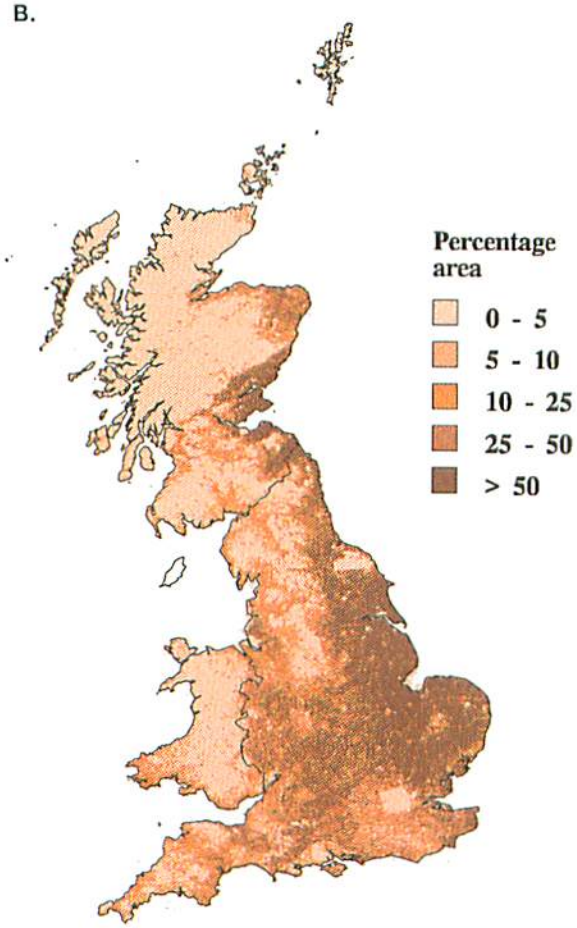
Figure 7.6

A. Distribution of AOT40 for agricultural crops for the period May to July using mean data for 1990-94.

B. Percentage area land cover of arable land, derived from the ITE Land Cover Map v1.0. Environmental Information Centre, ITE.

C. Exceedance of 3000 ppb h for arable crops. Environmental Information Centre, ITE.

B.



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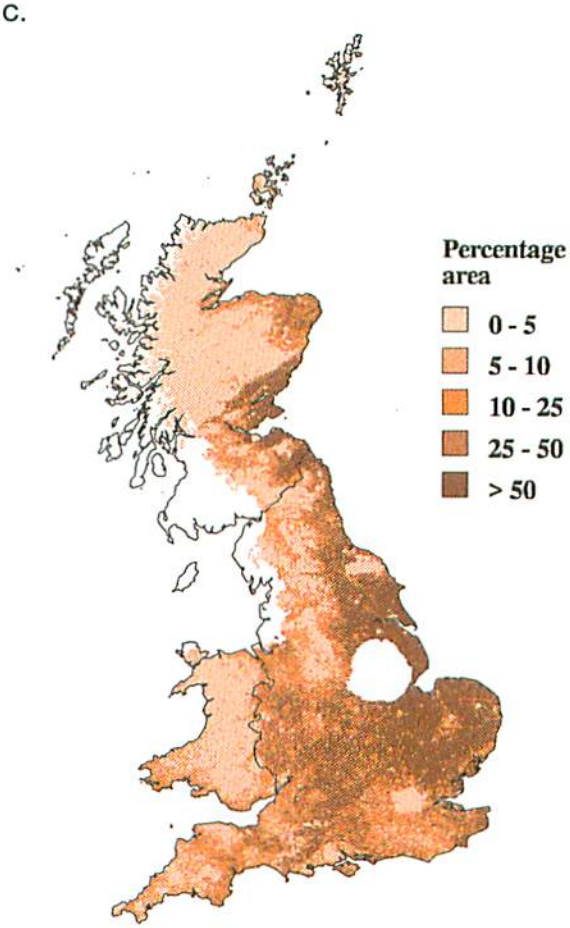

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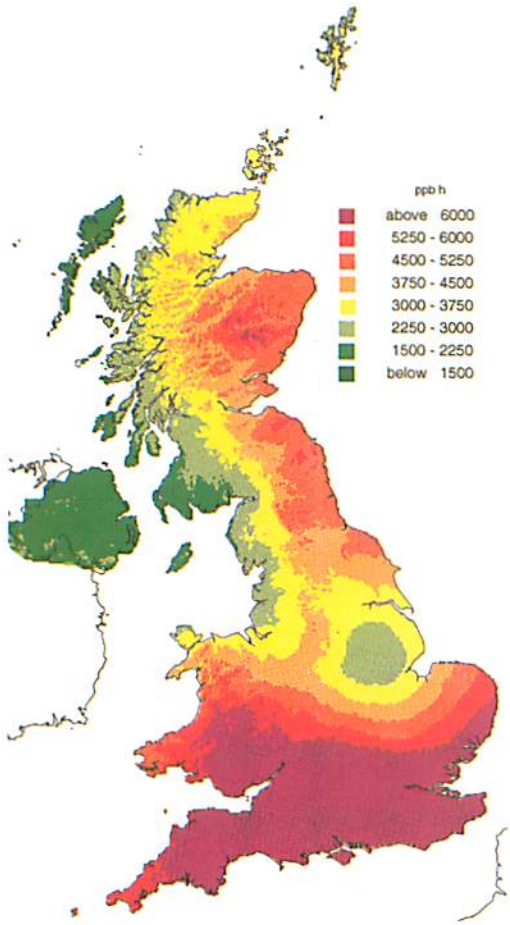


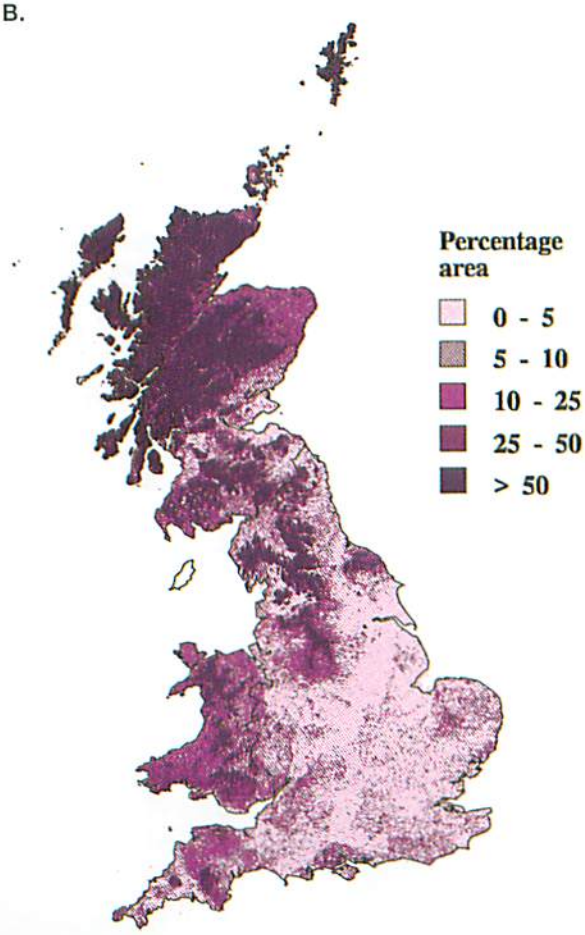
Figure 7.7

A. Distribution of AOT40 for semi-natural vegetation for the period May to July using mean data for 1990-94.

B. Percentage area land cover of semi-natural vegetation, derived from the ITE Land Cover Map v1.0. Environmental Information Centre, ITE.

C. Exceedance of 3000 ppb h for semi-natural vegetation. Environmental Information Centre, ITE.

B.



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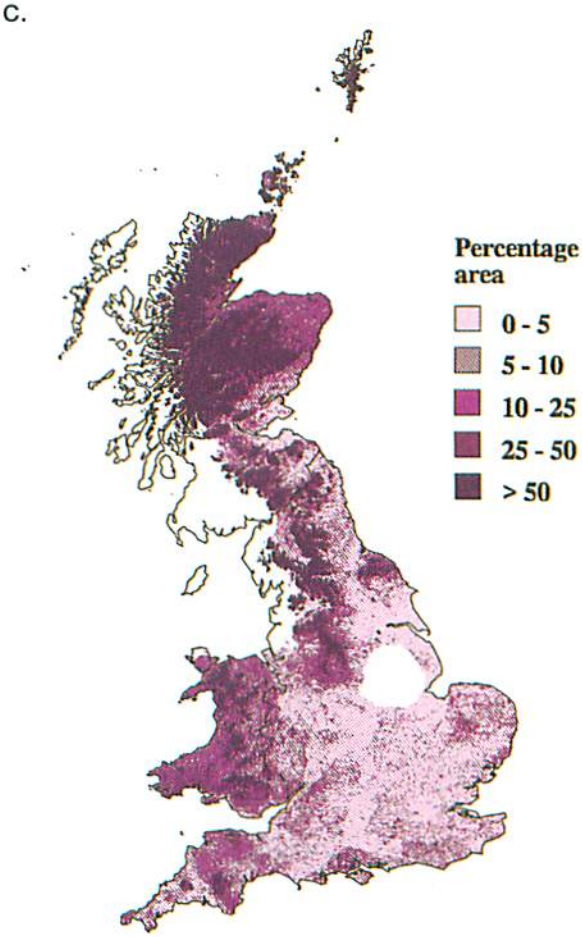


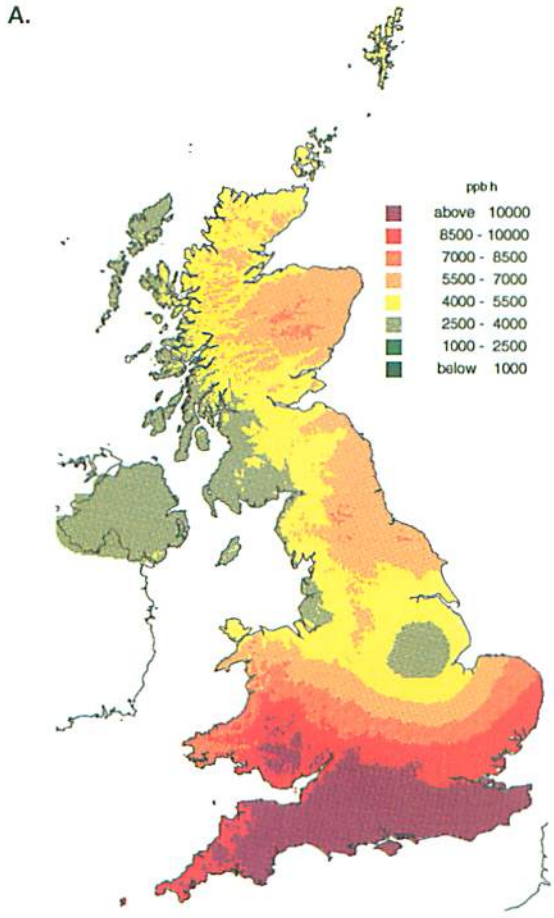
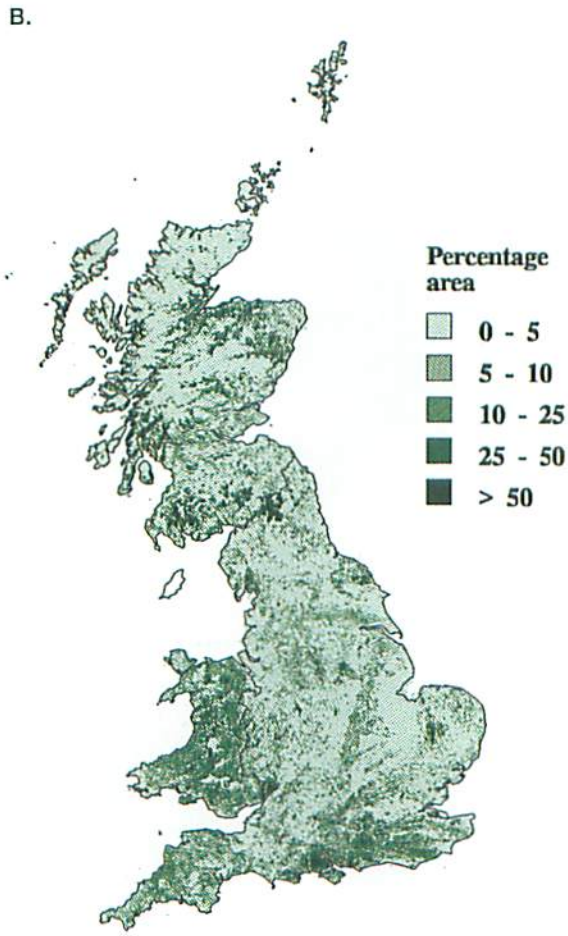


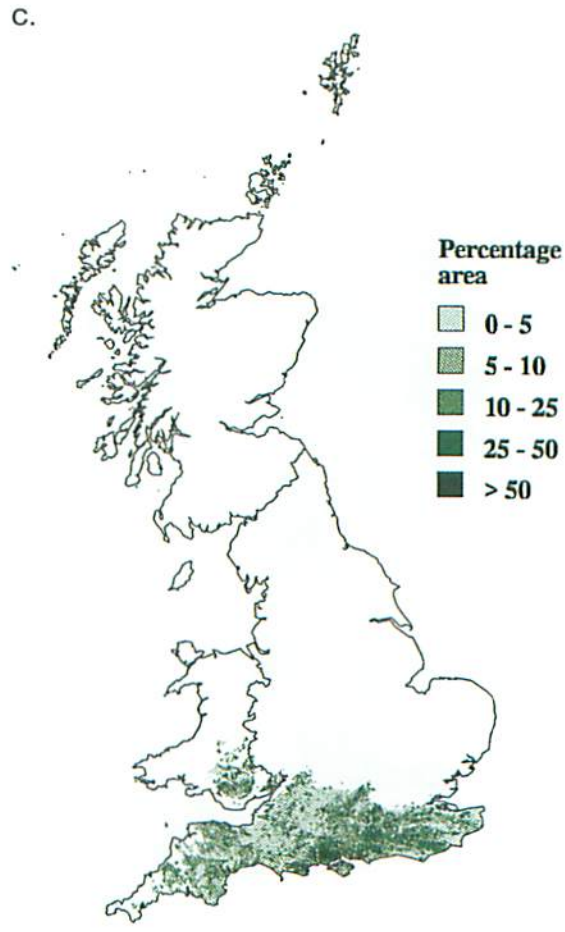
Figure 7.8

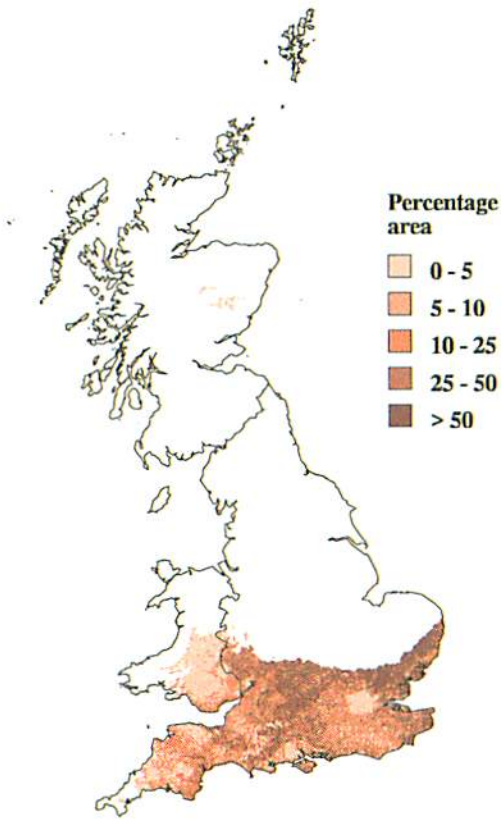
A. Distribution of AOT40 for forest for the period April to September using mean data for 1990-94.

B. Percentage area land cover of forest, derived from the ITE Land Cover Map v1.0. Environmental Information Centre, ITE.

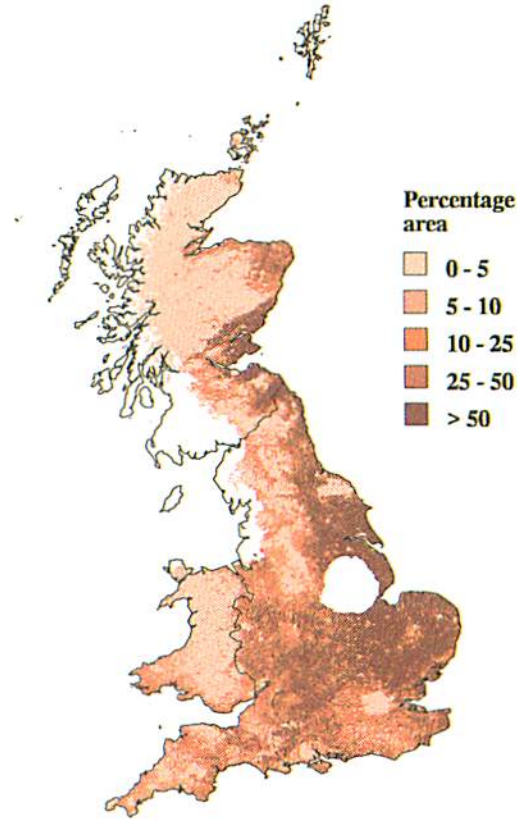
C. Exceedance of 3000 ppb h for forest. Environmental Information Centre, ITE.





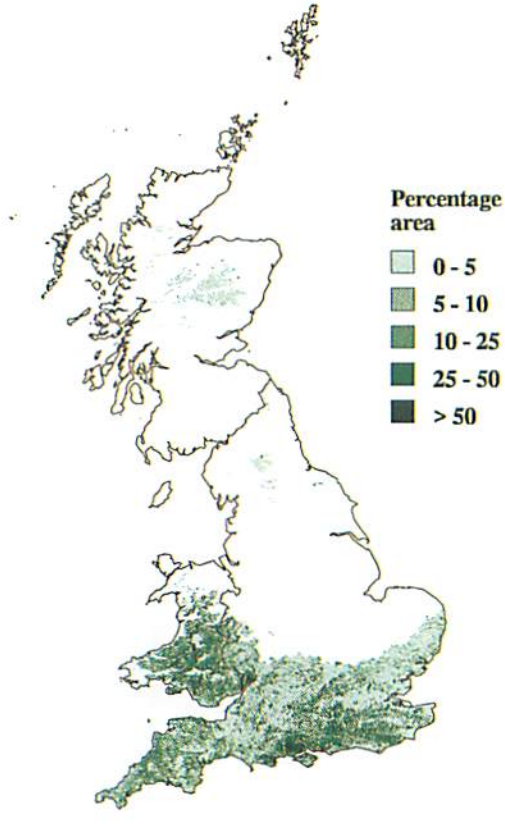


A.

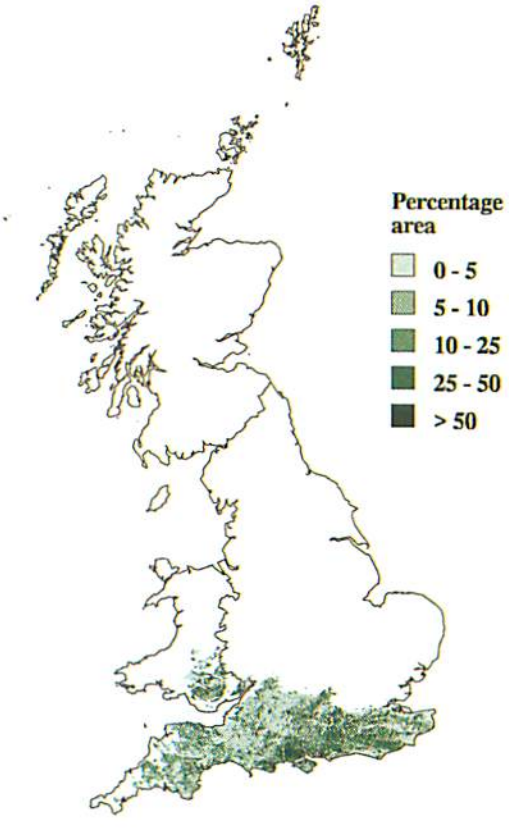


B.

Figure 7.9 Comparison of critical level exceedance maps for arable crops based on the recommendations of (a) the Bern workshop and (b) the Kuopio workshop. Maps provided by Environmental Information Centre, ITE.



A.



B.

Figure 7.10 Comparison of critical level exceedance maps for forest trees based on the recommendation of (a) the Bern workshop and (b) the Kuopio workshop. Maps provided by Environmental Information Centre, ITE.

there are a number of uncertainties in assessing the implications of exceedance of AOT40 critical level in terms of actual impacts on vegetation.

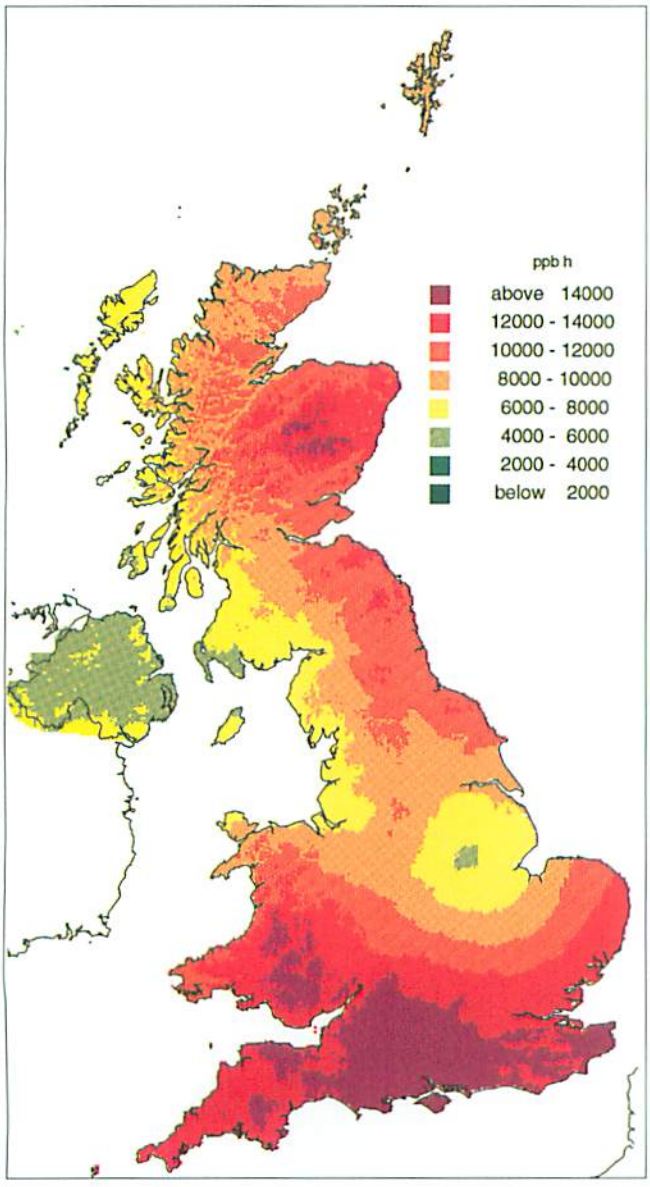
The following section considers these uncertainties, and their implications in the UK, further.

7.1.4 Key Uncertainties in Applying Ozone Critical Levels

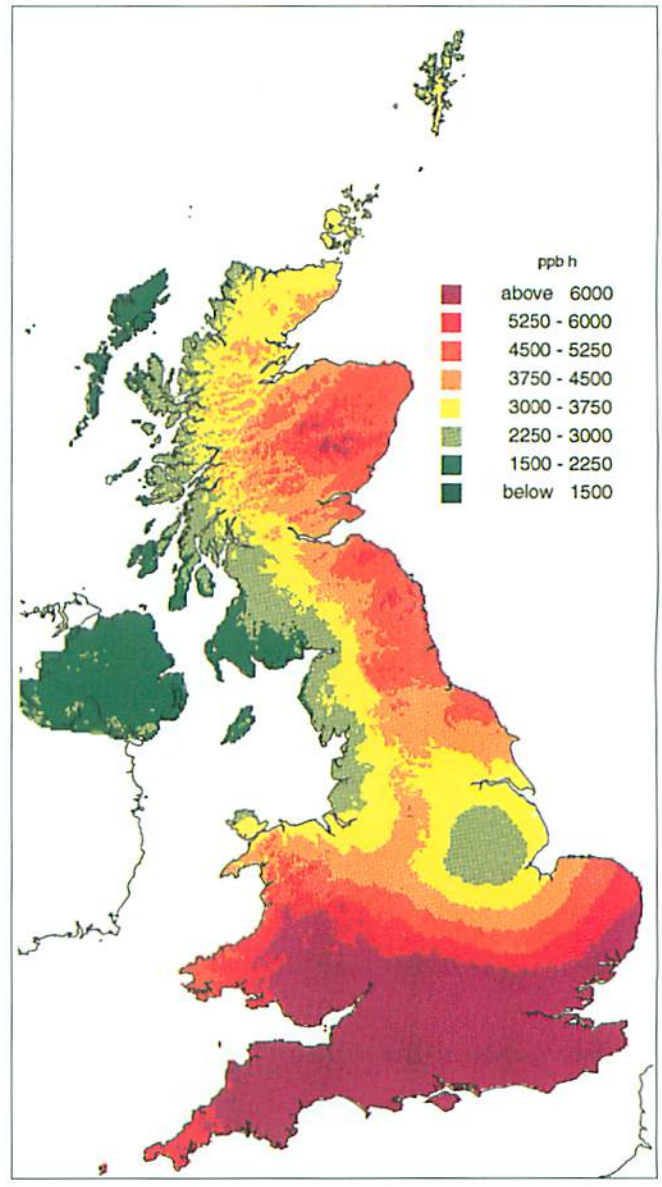
7.1.4.1 The Cut-off Concentration

Currently, the critical level for ozone is defined on the basis of the accumulated exposure above 40 ppb (AOT40). However, Fuhrer (1994) found that, for the exposure-response relationships for wheat, there is little difference statistically between using the AOT40 and AOT30 indices; indeed, for wheat the correlation coefficient using AOT40 is marginally worse than that using AOT30. Further analysis of wheat data by Pleijel (1996), including additional experiments from Nordic countries, showed almost identical correlation's for AOT40 and AOT30. The primary reason for adopting 40 ppb, rather than 30 ppb, at the Bern and Kuopio workshops was not biological, but was related to the view that 40 ppb represented the upper range of 'natural background' ozone and that it was the boundary above which ozone production was primarily due to European anthropogenic precursor emissions.

However, although the correlation coefficients for wheat exposure-response relationships are similar, the slopes of the lines are not identical, with the analysis of European data by Pleijel (1996) showing that the ratio of the slopes of the lines for AOT40 and AOT30 was 1.24. Pleijel (1996) also showed that, although the two lines predicted similar yield losses from the experimental data points when the AOT40 and AOT30 values were high, at low exposure values, the predicted yield losses were always higher when AOT30 values were used.



AOT30, May - July daylight hours.



AOT40, May - July daylight hours.

Figure 7.1 Comparison of maps of AOT40 and AOT30 for wheat, for period May-July using mean data from 1990-1994.

Table 7.1 Comparison of AOT40 Apr-Sept during 24 hours and daylight hours Mean of 1990 - 94, values scaled to 100% datacapture only in years when it exceeds 60%.

National Network Site	24 hours	daylight hours	difference	% daylight/24hr
Great Dun Fell	11827	7345	4481	62
Mace Head	7579	4671	2908	62
Aston Hill	11655	8002	3653	68
High Muffles	10434	7306	3128	70
Lullington Heath	16668	11671	4997	70
Strath Vaich	9431	6659	2773	71
Wharleycroft	8430	6190	2240	74
Bush	3242	2455	787	76
Sibton	12845	9738	3106	76
Yarner Wood	14429	10823	3606	76
Ladybower	6489	5183	1307	80
Eskdalemuir	5496	4462	1034	81
Lough Navar	3593	3039	553	86
Harwell	10942	9660	1283	89
Bottesford	3283	2975	307	92
Glazebury	4025	3758	268	94

There is also evidence that ratios of AOT40 to AOT30 at monitoring stations in Europe are consistently above 1.24, and this, together with the analysis of Pleijel (1996), suggests that the area of exceedance based on an AOT30 critical level may be greater than that based on an AOT40 critical level. This will particularly be the case for countries like the UK, where AOT40 values are relatively small.

The implications of using a 30 ppb, rather than a 40 ppb cut-off concentration have been examined for the UK (Figure 7.11). This analysis is based on the critical levels for crops only. For forest trees, similar geographical patterns might be expected, but since the critical level is not based on actual exposure-response relationships, it cannot be readily recalculated as an AOT30 critical level. The mapping procedure used to define the AOT40 field was applied successfully to the mapping of AOT30, indicating the potential for this alternative index to be used in mapping exercises. The geographical distributions of the two indices are broadly comparable, with the north-south gradient, the effect of altitude, and the reduced exposures in East Anglia, all being apparent.

Although the geographical pattern is similar to that for AOT40, the implications for exceedance of critical levels may be quite different. On the basis of the ratio of slopes derived by Pleijel, the critical level, as an AOT30, to prevent 5% yield reduction is approximately 4000 ppb h. On the basis of the map in Figure 7.11, this value is exceeded throughout the country. Thus the use of the AOT30 index leads to increase in the area of the country in exceedance of the critical level for crops.

This situation in the UK is similar to that in Scandinavia, and it has been argued, by Scandinavian scientists in particular (Skarby *et al,* 1994), that the 40 ppb cut-off is too high, and that there is evidence of impacts of ozone at locations where a concentration of 40 ppb is rarely exceeded. The choice of 40 ppb rather than 30 ppb as the cut-off concentration will also have implications for the effectiveness of different control strategies; the use of 30 ppb would tend to increase the value of emphasising NO_x control rather than VOC control. It is hence essential that further, specifically designed experiments are carried out to determine the significance of exposure to ozone concentrations below 40 ppb, since retrospective analysis of existing exposure-response data is unable to distinguish which cut-off is most appropriate.

7.1.4.2 Measurement Height

The critical levels of ozone set at the Bern workshop were derived from experimental data on crops and young trees exposed in open-top chambers. In these chambers, there is forced ventilation of air to ensure uniform mixing of pollutants and to minimise ingress of ambient air. Ozone concentrations are typically measured at a location immediately above the crop or adjacent to the trees.

In contrast, measurements of ozone in the UK national network are typically made at an inlet height of 2-3 m, which is well above the height of most arable crops, grasslands, and many types of semi-natural vegetation. The question arises as to whether these values, and in particular the calculated values of AOT40, are comparable to those at the surface of the vegetation to which the critical levels actually apply?

Analysis of measurement data over a barley field in Sweden (Pleijel *et al,* 1995) shows substantial gradients of AOT40 over a short vertical distance. Ozone concentrations were measured at 9 m, 5 m, 2 m and 1 m above the ground over a crop which was 0.7 m tall. The results show a decrease in AOT40 from about 2000 ppb h at 9 m to 800 ppb h at crop height (Figure 7.12). This indicates that, for crops, the effect of measurement height may be substantial, potentially resulting in a considerable error in the estimation of critical level exceedance. Comparing estimated Swedish values measured at 3 m with those at crop height, it is likely that the mapped values based on the UK national network height could overestimate the actual AOT40 at crop height by about 80%.

This issue has also been addressed using deposition models. Tuovinen & Laurila (1993) calculated seasonal AOT40 values at 0.1 m compared with those measured at 5 m. The calculated value at 0.1 m was 2550 ppb h, compared with 6450 ppb h at 5 m, and 8550 ppb h at 50 m, the height in the boundary layer used in the EMEP model. This was despite the fact that the differences calculated in seasonal mean concentrations are quite small. This is because at the location in Finland for which the calculations were carried out, a substantial part of the annual AOT40 is made up of frequent exposure to concentrations in the range of 40-50 ppb; thus a small decrease in mean concentrations can have a large impact on AOT40 values.

A similar calculation has been carried out for a UK moorland site, with a model generating the vertical profile, shown in Figure 7.13, from ozone measurements made at ~3 m. The conclusions are broadly similar to those of the Swedish and Finnish studies. There is a steady fall in AOT40 with height from 10 m to 2 m, and then a rapid decrease within the 1 m close to the vegetation height of 0.2 m. The AOT40 calculated at 3 m was almost exactly twice that at the actual height of the vegetation.

Thus, there is the potential for very substantial over-estimates of the extent of critical level exceedance for low-growing vegetation such as grassland, moorland and arable crops. For estimates based on measurement networks the three studies suggest an error of around 100%. However, all three studies were from relatively northerly locations, where AOT40 is dominated by chronic exposure to relatively low concentrations. The effect at more southerly locations where episodic exposure is more important may be smaller in size, and it would be unwise to apply any corrections until this issue has been investigated further.

Furthermore, the vertical gradient over the vegetation measured in these studies may differ significantly from that at individual monitoring stations in the UK network, since very local topography and meteorology will affect how similar the AOT40 at measurement height is to that above local vegetation surfaces. Thus, until such local features are more thoroughly examined, it would be unwise to make calculations over the network to correct for this height effect.

For forests and other aerodynamically rough vegetation, this issue is of less concern. Substantial variations in ozone concentration with height immediately above the vegetation would not be expected, and Pleijel *et al* (1995) found no significant differences between measurements at the same height inside and outside a mature spruce stand. Thus measurement-based maps should provide a relatively accurate indication of the exposure experienced by mature forests.

7.1.4.3 Night-Time Exposure

The crops group at the Bern and Kuopio workshops defined the critical level on the basis of daytime exposures only. This is because the flux of ozone into the leaf is controlled by stomatal uptake; since the stomata in most species and situations close in the absence of light, this flux essentially becomes zero during the night. Hence any ozone exposure during the night is likely to have little or no biological impact and is ignored in determining exceedance of the critical level.

However, a very different approach was taken by the forests group at Bern. Here, it was argued that there is some evidence of stomatal uptake at night in certain tree species. While others argued that this was not the case in most species and situations, it was decided that on a precautionary principle, the ozone critical level

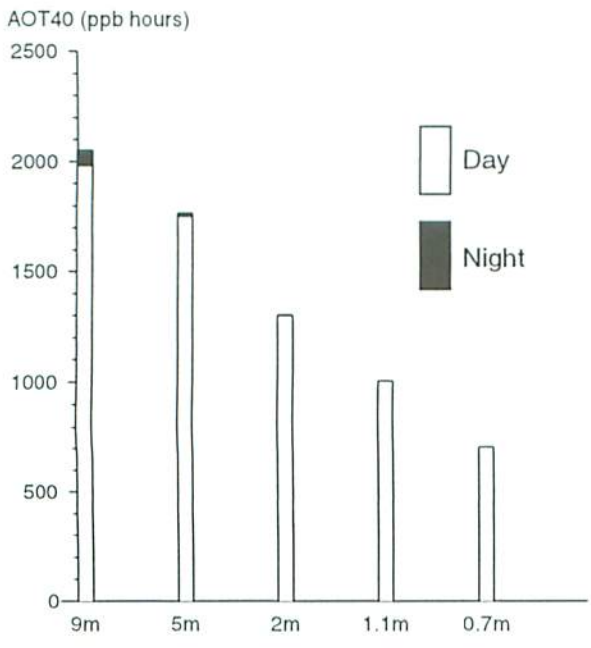


Figure 7.12 Measured vertical profiles of AOT40 over a barley field in southern Sweden. From Pleijel *et al* (1995).

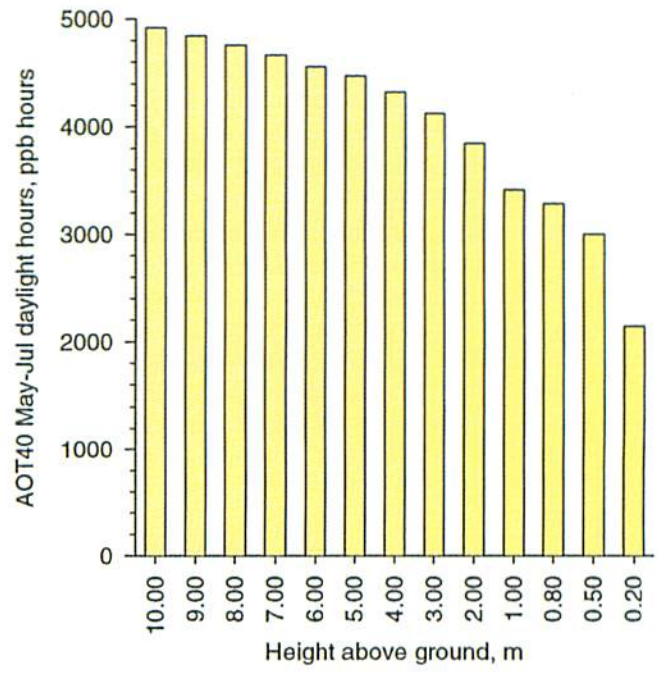


Figure 7.13 Vertical profiles of AOT40 over a moorland site in southern Scotland.

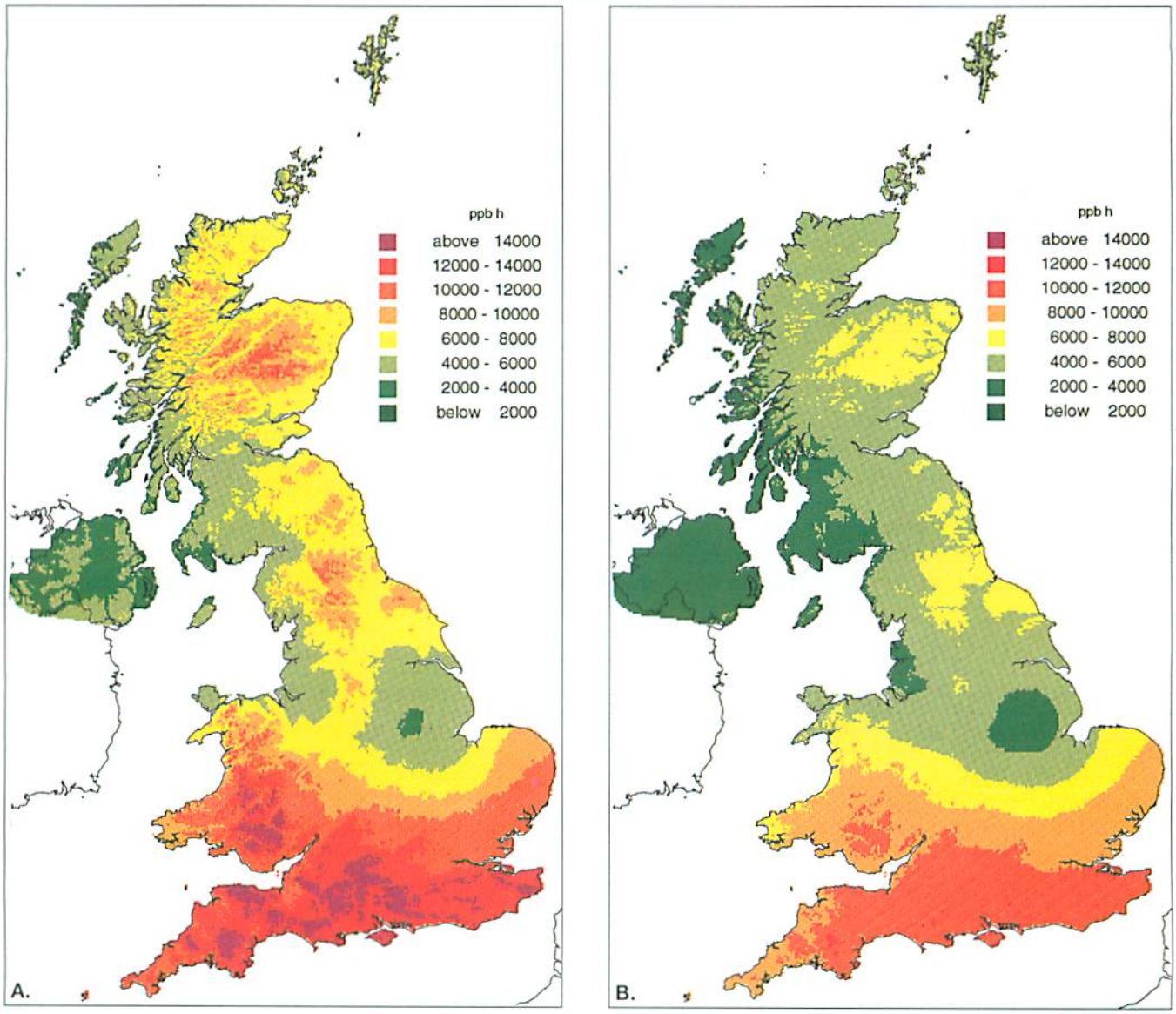


Figure 7.14 Comparison of AOT40 maps for forest trees, calculated using data for (a) 24 hours and (b) daylight hours only. Data are for April-September for the period 1990-94.

should also consider night-time exposure. This decision was reversed at the Kuopio workshop, where it was decided that, even if some stomatal uptake of ozone were evident, night-time uptake was likely to be small compared to that during the day.

The implications of using the daylight hours basis, rather than 24 hours, for the UK have been examined using the PORG database (Table 7.1). There is at every site a significant night-time component to the seasonal AOT40. The proportion of total AOT40 which is the daylight hours varies substantially between sites, from 62% at Mace Head to 94% at Glazebury. In general terms, it is the more remote and high elevation sites which show the lowest proportion in daylight, and hence for which the uncertainty over night-time uptake is most significant. However, in absolute terms, large differences in AOT40 are found at southern sites, such as Lullington Heath and Yarner Wood, as well as at the remote and high elevation sites.

Figure 7.14 shows a forest AOT40 map for the five-year mean values, calculated using a 24 hour basis and using the daylight hours basis. The percentage of the UK land area in exceedance of the critical level for ozone decreases substantially when the daylight hours approach is used, from 30% to 15%. It is the areas in the midlands and north of England, and in Wales, which are no longer in exceedance, including several upland areas with extensive forest cover. This is consistent with data in Table 7.1, showing that at five sites in this area (Aston Hill, High Muffles, Great Dun Fell, Sibton and Harwell) the mean AOT40 is above the critical level when calculated on a 24 h basis, but not when calculated on a daylight hours basis.

The change in the geographical distribution of exceedance shown in Figure 7.14 is broadly similar to that in Figure 7.10, in which the maps based on the Kuopio and Bern meetings were compared. This indicates that of the two changes made at the Kuopio workshops - to use the 5-year mean rather than the worst year in five, and to change from 24 hours to daylight hours - it is the latter which has the greatest impact on exceedance maps in the UK.

7.1.4.4 Annual Variation

As was shown above, the changes in the methods of calculating critical levels and their exceedance between the Bern and Kuopio workshops have significantly altered the area of the UK in exceedance of the critical level of ozone for crops. One key factor in this was the change in the AOT40 values for comparison with the critical level from the worst year in the past five, to the mean AOT40 over five years. From a statistical standpoint, mapping the AOT40 averaged over several years has considerable attractions, since the data are more robust and should represent the average spatial distribution over the UK.

However, this decision does not necessarily resolve some of the problems, in terms of assessing ozone impacts on vegetation, which are induced by the fact that ozone concentrations can vary dramatically from year to year, depending on climatic conditions. For annual crops, each year of exposure can be considered independently, but the situation is more complex for trees and other long-lived perennial species. Over a five year period, a tree may experience the same total AOT40, through five years of relatively constant ozone exposure or through a mixture of years of high or low exposures. These may not have the same biological consequences, since exposure to ozone in one year is known to have adverse carry-over effects on metabolism and growth in the subsequent year both in trees and in herbaceous species such as clover (e.g. Rebbeck *et al*, 1988). Furthermore, historical growth studies, for example of beech in southern Britain, have show that single years with high stress conditions, such as the hot, dry (and high ozone) summers of 1975 and 1976, may reduce subsequent shoot growth over a period of up to one decade (Power, 1993).

The PORG database can be used to explore the variation in AOT40 values from year to year at individual sites. Table 7.2 shows data for 16 monitoring sites for the 8 year period 1988-1995.

In the case of crops, the sixteen sites neatly fall into two almost equal groups. At seven of the sites, the critical level of 3000 ppb h was only exceeded in two

Table 7.2 Annual AOT40 values for 16 national network sites.

National Network Site	1988	1989	1990	1991	1992	1993	1994	1995	Average
a. AOT40 for wheat (daylight hours May-Jul), years with datacapture over 60% scaled to 100%									
Strath Vaich	3758	3231	3474	4871	5989	2476	5088	2048	4127
Bush, Penicuik	3171	3993	2461	436	3179	587	1826	1538	2236
Eskdalemuir	2274	5398	3939	1685	5076	2108	3343	3415	3403
Lough Navar	2472	4022	3502	1123	3712	790	1358	1974	2426
Great Dun Fell	5118	8672	5558	3024	9860	3194	4726	4526	5736
Wharleycroft	2496	7207	3577	4765	5203	3385	3991	5482	4375
High Muffles	3370	9255	4753	4212	7778	3770	5725	4522	5552
Mace Head	1924	4114	3970	2512	3133	2053	2236	2916	2849
Glazebury		2825	3372	2240	4919	1586	2026	2276	2828
Lady Bower Reservoir		8431	5640	2554		2564	4100	4477	4658
Bottesford	443	3227	3187		2076	1921	1878	2175	2122
Aston Hill	5018	7442	9245	2339	6854	3683	5833	5407	5774
Sibton	3614	9148	4775	4279	9450	6067	8378	5684	6530
Harwell	726	7029	7236	3704	9729	4803	9344	6597	6082
Lullington Heath	3719	13074	8955	3271	11432	6621	8263	10050	7905
Yarner Wood	1860	13774	9961	4690	10180	4372	5117	7212	7136
b. AOT40 for forest (Apr-Sept daylight hrs) years with datacapture over 60% scaled to 100%									
Strath Vaich	4918	4192	4829	8454	7764	4649	7597	4820	6058
Bush, Penicuik	3546	4603	3937	1210	3786	902	2441	2181	2918
Eskdalemuir	2837	6522	5745	3579	5792	3156	4040	5898	4524
Lough Navar	3214	4648	4138	2927	4814	1229	2090	3789	3294
Great Dun Fell	6555	9137	8368	5768	11631	5294	5664	8448	7488
Wharleycroft	3499	7071	5656	9460	5797	5130	4908	10283	5932
High Muffles	4830	9899	6953	8092	9058	5131	6854	7583	7259
Mace Head	2352	5285	5719	6094	3843	3631	4068	6544	4427
Glazebury		3396	4668	4008	5381	2355	2376	4961	3697
Lady Bower Reservoir		9370	8038	3875		3932	4886	7145	6020
Bottesford	943	3684	5541		2441	1729	2190	5086	2755
Aston Hill	7020	8501	12995	5944	8282	5130	7658	11301	7933
Sibton	6236	12956	9597	8364	11578	8977	10175	8905	9698
Harwell	1761	10496	10995	9308	11930	6069	9996	12894	8651
Lullington Heath	6776	17034	17377	7571	13543	9051	10811	15472	11738
Yarner Wood	3647	16767	16506	12124	12326	6788	6372	13738	10647

or three years, indicating that years with ozone levels potentially high enough to affect crops yield are relatively infrequent. These include remote sites in Scotland and northern Ireland, but also sites in agricultural areas of England (e.g. Bottesford and Glazebury), both of which are probably significantly affected by high NO_x emissions. At the remaining nine sites, the value of 3000 ppb h was exceeded in six or more of the eight years, indicating a consistent potential for effects on crops.

For forests, the situation is very different. At ten of the sixteen sites, there was no year in which the critical level of 10000 ppb h is exceeded, and at two other sites it was only exceeded in one of the eight years. Only at the four most southern sites were there between three and five years with AOT40 values above the critical level. The significance of occasional years of high ozone exposure at sites like Aston Hill and Sibton, where the long-term mean AOT40 is below the critical level, is uncertain, but the could indicate a potential for adverse effects on tree growth.

It may also be the case that it is not just the overall ozone levels which vary from year to year; the spatial pattern of ozone exposure may also be different. To explore the stability of the spatial patterns, the AOT40 maps produced for the five-year mean period (1990-1994) have been compared with those for three recent individual years:- a relatively high ozone summer (1989); an intermediate summer (1992); and a relatively low ozone summer (1993). Figure 7.15 shows the resultant maps for crops while Figure 7.16 shows a similar comparison for forests.

Considering the geographical variation in AOT40 values, for both crops and forests, the five-year mean and the three individual years have some broad features in common. In particular, there is a general north-south gradient in AOT40, with the southern part of England and Wales consistently recording among the highest exposure values. There is an area of East Anglia which consistently records relatively low AOT40 values, compared to the surrounding area.

However, there are also some important differences, which would significantly alter the assessment of ozone impacts on arable production and forest growth. In particular, the location and size of the area of East Anglia where the critical level is not exceeded is quite different. One factor here may be the relatively high AOT40 values in 1989 and 1992 at sites to the north and west, which makes the 'hole' of low values in East Anglia more apparent; in contrast, AOT40 values to the north and west were relatively low in 1993.

Finally, it should be noted that the interpretation of year-to-year variations in AOT40 in terms of actual impacts should be made with caution. For example, Brown *et al* (1996) compared AOT40 values for two summers (1988 and 1989); whereas AOT40 values were higher throughout the UK in 1989, the accumulated soil moisture deficit was also much greater in 1989. Thus ozone uptake into vegetation may have been limited by stomatal closure in the warmer, drier year of 1989, and it cannot be assumed that the actual impacts of ozone were greater in that year.

7.1.4.5 Seasonal AOT40 Patterns

Although there is evidence of linear responses to AOT40 in experimental situations, these are often somewhat artificial, in that ozone is added at relatively constant concentrations on every appropriate day. However, in practice, real seasonal ozone exposures may be much more stochastic and episodic. This raises important issues, since the timing of episodes may affect their impact, as the stage of phenological development of a plant may affect its sensitivity. Furthermore, it is of importance to understand the extent to which real AOT40 exposures in the UK are made up of short acute episodes of relatively high concentrations, or longer term exposures to relatively low concentrations.

Figure 7.17 shows the seasonal pattern of daily AOT40 exposures at eight network sites, representing the range of conditions over the UK, during 1992, based on the forest growing season. These plots provide a rapid visual indication of the nature of the exposure patterns, with the sites arranged along a north-south gradient. In terms of the days with maximal AOT40 values, there seems to be little difference between the six English sites, at which the maximum daily value was about 700 ppb h (equivalent to a concentration of 110 ppb for 10 h). In contrast, the maximum daily values at the two Scottish sites were around 250 ppb h, half the values at other sites. In terms of the numbers of episode days, again there appears to be little difference between the English sites, but that certain key episodes of high AOT40, such as that in late June, were not seen at the Scottish sites. The differences in seasonal AOT40 values between the English sites appears to derive, at least in this year, primarily from differences in the frequency of days with relatively high AOT40 values, i.e. above 300 ppb h, which is equivalent to 70 ppb over 10 hours.

Figure 7.17 shows that in 1992, at all eight sites, the major part of the seasonal AOT40 was concentrated in the period from early May to early July; relatively little additional AOT40 was accumulated during July, August and September. In this type of year, the impact of ozone on wheat, for example, may be substantial, since it is concentrated in the period when the crop is likely to be most sensitive.

To examine how variable the seasonal AOT40 pattern is from year to year, the development of the AOT40 index over the course of a six-month period in the four years,1989, 1991, 1992 and 1993 is shown in Figure 7.18 for the same eight sites. The timing of the period of greatest AOT40 is indicated by the periods with the greatest slope. The data broadly suggest that in two years (1992 and 1993), the pattern was rather similar, with most of the AOT40 experienced in the months of May and June, and little additional exposure during the period July to September. In contrast, in 1991, there was little AOT40 accumulated in May or June, and most of the AOT40 was in accumulated in April, July and August. In certain cases, years giving the same total AOT40 at a site show completely different seasonal patterns (e.g. 1991/1992 at Yarner Wood; 1989/1991/1993 at Wharleycroft; 1989/1991/1993 at Great Dun Fell).

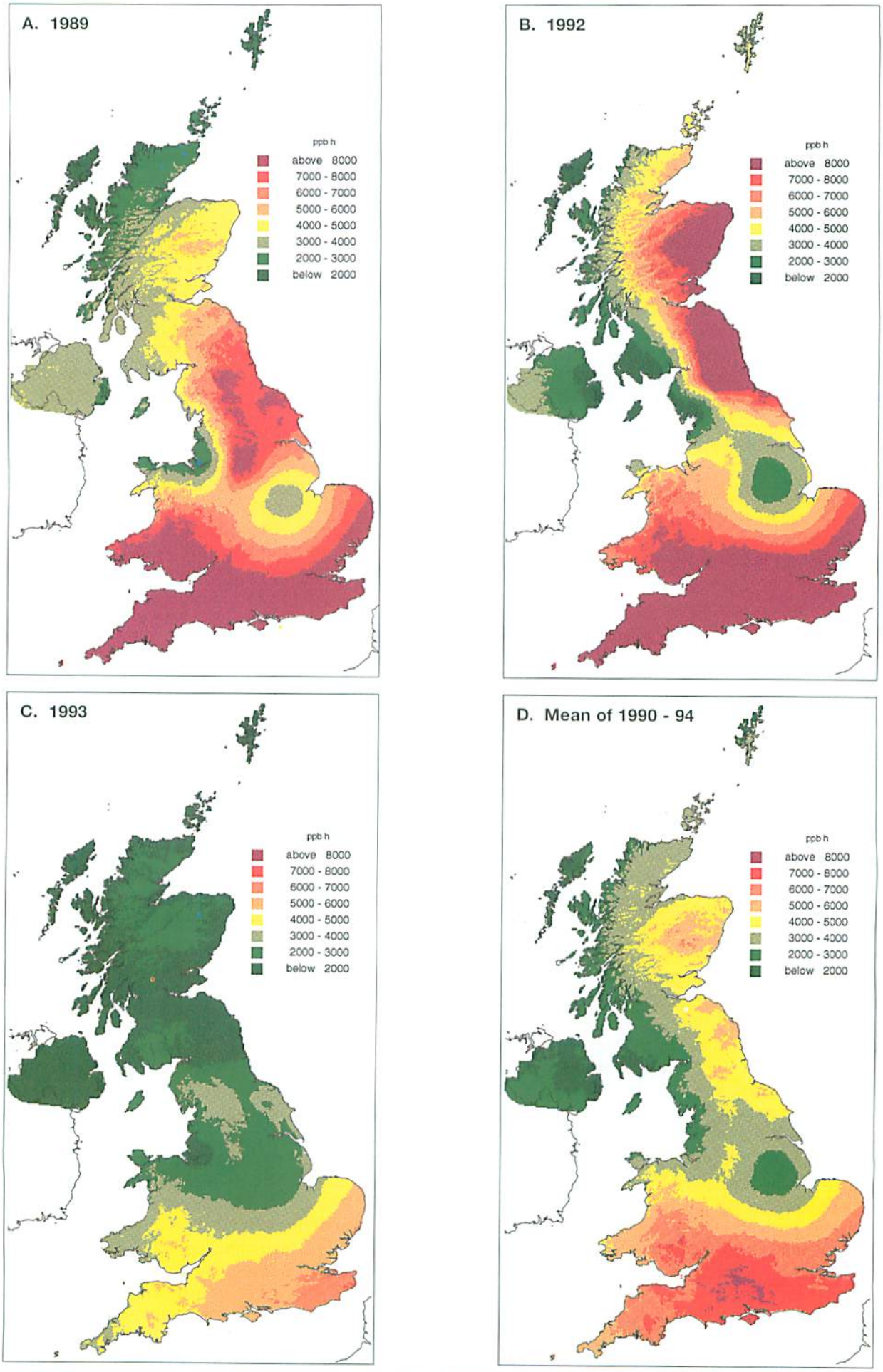


Figure 7.15 Comparison of distribution of five-year mean AOT40 values for agricultural crops with those for three individual years.

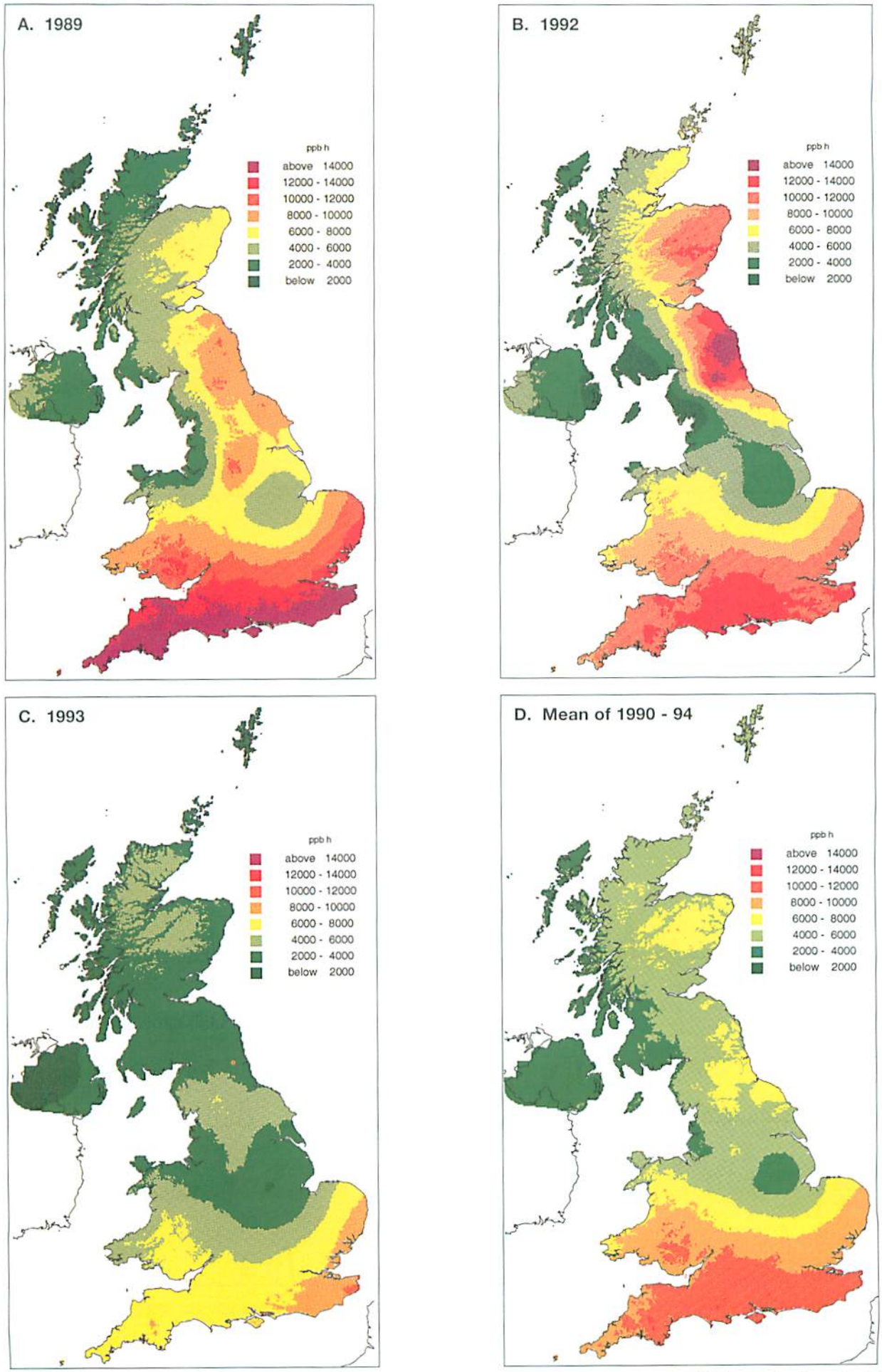


Figure 7.16 Comparison of distribution of five-year mean AOT40 values for forest trees with those for three individual years.

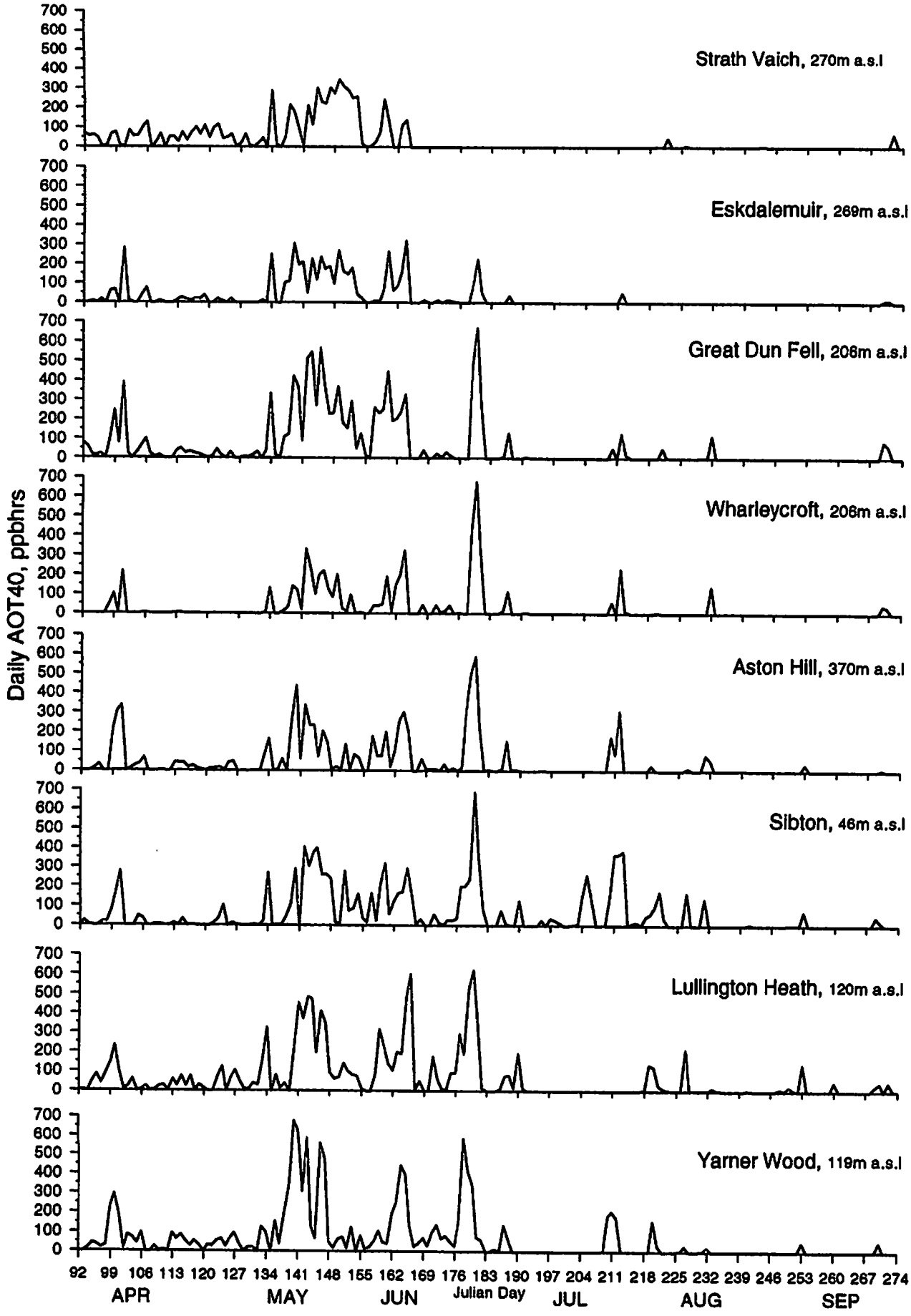


Figure 7.17 Seasonal patterns of AOT40 values, during daylight hours, at 8 rural monitoring sites for 1992.

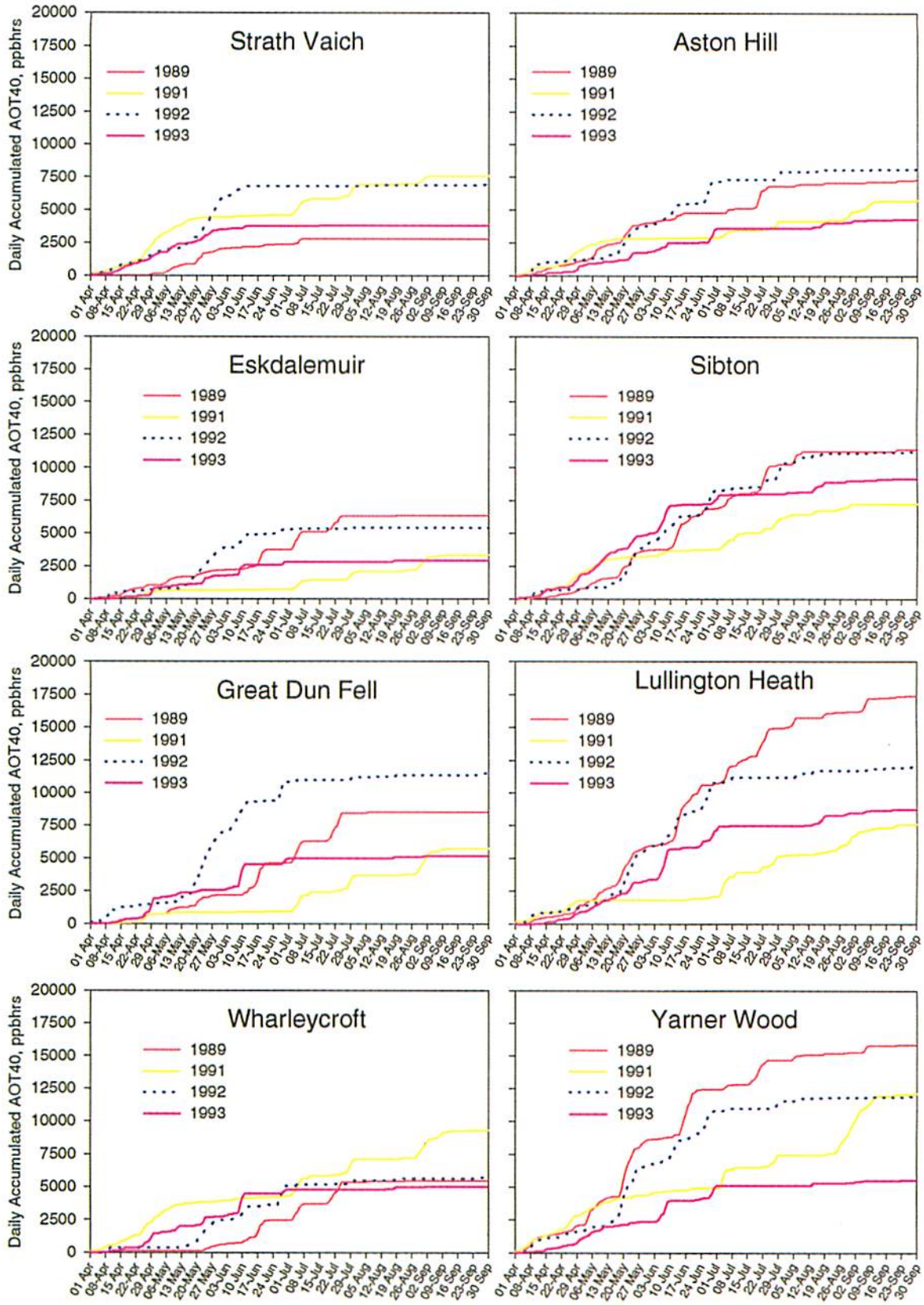


Figure 7.18 Seasonal development of cumulative AOT40, during daylight hours, at eight rural monitoring sites for four individual years.

Because of phenological variation in plant sensitivity, these differences in seasonal pattern could have led to quite different impacts on vegetation, even though the annual AOT40 values were quite similar.

At certain sites shown in Figure 7.18, the seasonal patterns are relatively consistent from year to year (e.g. the majority of the exposure at Strath Vaich is always in April and May). In contrast, other sites show very large differences from year to year. To assess whether there are consistent differences in seasonal patterns between the eight sites, mean data for the period 1990-1994 were examined (Figure 7.19).

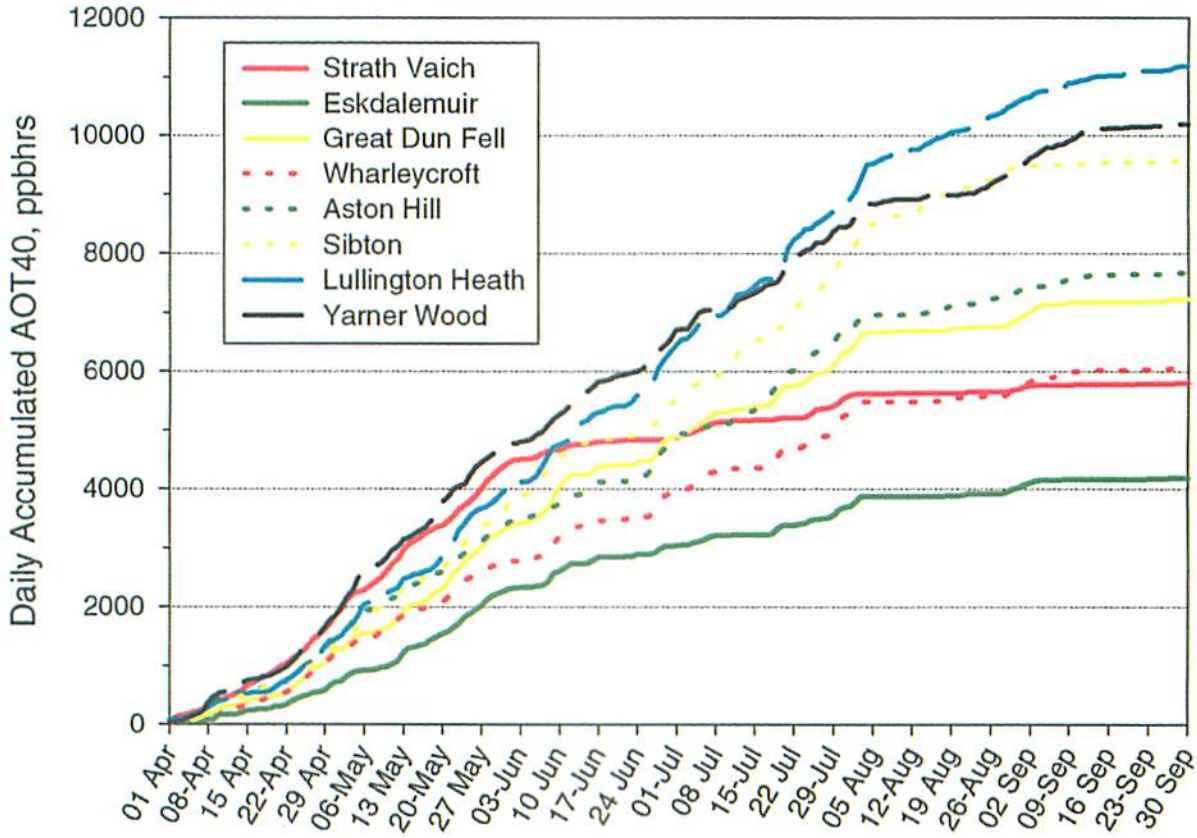


Figure 7.19 Seasonal development of cumulative AOT40, during daylight hours, at eight rural monitoring sites using mean data for the period 1990-94.

Broadly speaking, seven of the eight sites show rather similar seasonal patterns, as indicated by the fact that their ranking changes little over the six months. The exception is the Strath Vaich site, at which the AOT40 accumulated over the period April-May is as high as that at the sites in southern England, but which shows the lowest accumulated AOT40 over the remainder of the year. This indicates that a very different source of ozone dominates the AOT40 index in this region of the country.

7.1.4.6 The Growing Season

As indicated above, the definition of the period to be used in calculating the cumulative exposure above 40 ppb is critical. If the period is too long, an artificially high AOT40 value will be calculated, which includes periods when the vegetation is not actually present or is dormant and taking up little ozone. If the period is too short, then too low a value will be calculated and periods when the vegetation is experiencing significant impacts of ozone may be omitted.

For the biologist, the easiest solution is to calculate the AOT40 value over the growing season, which would be spatially variable, depending on land use and climate. However, a fixed growing season was adopted at the Bern and Kuopio workshops because of a perceived need in the mapping community for consistent and readily defined time periods.

For crops, the period of interest is largely defined by the local cropping patterns. For wheat, the adoption of the three months of May, June and July seems reasonable for the UK. However, when the AOT40 is applied to UK arable agriculture in general, and not just to spring wheat, the situation becomes more complex, since the growing seasons of other crops, such as rape and potato, may be quite different. Thus while the current methods used in the evaluation of critical level exceedance provide a general risk assessment for the UK, the use of a fixed May-July period may lead to misleading conclusions, depending on the local crops. A more detailed analysis of cropping patterns in relation to seasonal ozone patterns would be needed to assess the significance of this factor for individual crops.

The effect of calculating the AOT40 for crops over different three month growing periods is summarised in Table 7.3 and Figure 7.20. The results for most sites, for the five-year mean AOT40 values, show that the May-July period contains either the highest AOT40, or AOT40 values similar to those in other 3-month periods. The only exceptions are the remote Mace Head and the Strath Vaich sites, where the mean AOT40 in the April-June period was about 1000 ppb h higher than that in the May-July period. It therefore appears that, with the exception of the two remote sites, the choice of the May-July period for the UK is consistent with the precautionary approach underlying the Level I critical level approach, and should ensure that maps do not show a lack of critical level exceedance in areas where adverse effects on crop yield may occur.

For forests, the situation is a little different, given the longer fixed growing season of six months which was adopted. For deciduous trees, producing a new set of

Table 7.3 Mean of 1990-94 3 Monthly Sums of AOT40

Rural Network Site	Apr to Jun	May to Jul	Jun to Aug	July to Sep
Strath Vaich	5031	3988	1484	1343
Bush	1684	1661	1087	731
Eskdalemuir	3132	3149	1872	1216
Great Dun Fell	4868	5136	3620	2312
Wharleycroft	3936	4129	3024	2137
Lough Navar	1969	2034	985	1027
High Muffles	4746	5087	3374	2265
Mace Head	3514	2688	1090	1003
Glazebury	2522	2589	1570	693
Ladybower	2410	3517	2909	2194
Bottesford	1348	2321	2459	1952
Aston Hill	4809	5301	4008	2868
Sibton	5299	6399	5628	4116
Harwell	5129	6101	5690	4389
Lullington Heath	6179	6509	6562	5604
Yarner Wood	6478	6601	5199	4371

leaves each year, a particular concern is how much of the seasonal AOT40 falls in the period of April and May which lies before budburst. This will depend on species, location and climate.

In the case of evergreen species, the situation is more complex. However, budburst produces a new set of needles which are likely to be more sensitive to ozone, but also increases the ozone flux to the older needles. Thus, a period of AOT40 values before budburst is still of concern. Nonetheless, significant ozone flux to older, over-wintered needles can occur in warmer days in March, and the possibility of additional significant exposure in this period, especially at the more remote sites, should not be excluded.

7.2 The Effects of Ozone on Materials

7.2.1 Introduction

In our previous reports (PORG, 1987, 1983) we have drawn attention to the fact that O_3 may affect certain materials as well as vegetation, health and climate. It has become clear that our knowledge of the economic significance of this is relatively poor (PORG 1983, Lee *et al* 1996). It has been stated that the effects of O_3 on materials are well known (Isaken, 1988). This is only partially true. That O_3 affects rubber, surface coatings and textiles has been known for some time (Newton 1945, Campbell *et al* 1974, Salvin 1969). However, very little research has been undertaken in the last twenty years or so into the incidence of effects on materials, the mechanisms of damage, the attribution of O_3 to damage in comparison to other factors, and economic evaluation of such damage.

Accordingly our knowledge of which materials are at risk, and the extent of damage, is far from complete. In this section we provide a short review of the materials affected by O_3, how they are damaged and the scale of potential costs of O_3 damage in the UK. A programme of research is now underway to address some of these problems, and the approaches taken are described.

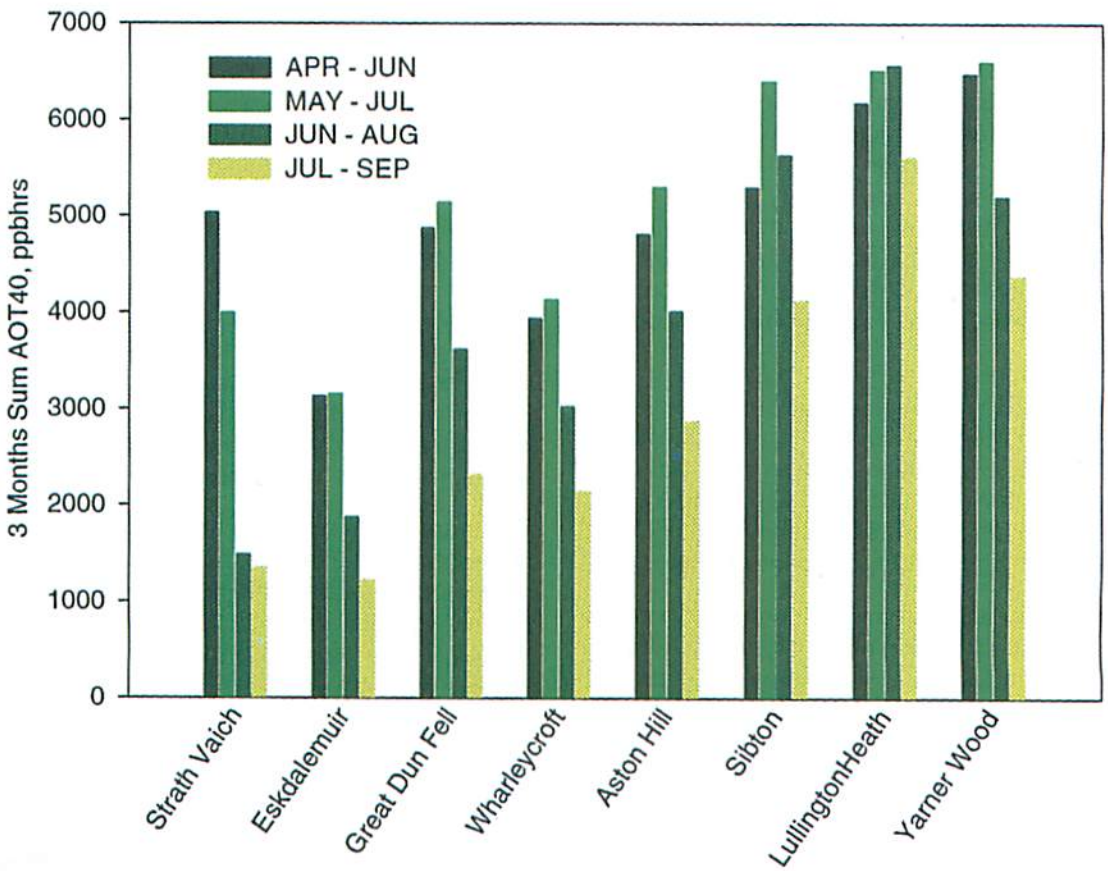


Figure 7.20 Comparison of three-month AOT40 values, during daylight hours, for four different periods of the summer at eight rural monitoring sites, using mean data for 1990-94.

7.2.2 Polymeric Materials and Ozone Damage

There is evidence that natural and synthetic rubbers and bulk polymers are affected by O_3. The types of rubber which are most susceptible to attack are those with main chain unsaturation. Natural rubber is more prone to damage from O_3 than synthetic products but those that are known to have some sensitivity include polyisoprene, polybutadiene, acrylonitrile-butadiene and styrene-butadiene. Of intermediate sensitivity are isobutene-isoprene and polychloroprene. The principal O_3-resistant rubber in general use is EPDM. The effects of O_3 on unprotected natural rubber and general-purpose diene rubber can be severe with cracks appearing within a few days at ambient concentrations as low as 10 to 30 ppb, independent of the action of UV radiation. Ozone attaches to the double bond between carbon atoms along the main chain to form an unstable molozonide, and the resultant chain scission is caused by rearrangement of the intermediate zwitterion. If the rubber is unstressed, this reaction takes place rapidly but the degradation only proceeds to a shallow depth, of the order of 0.5 m. This results in a white bloom or frosting on transparent or coloured surfaces.

However, if the rubber is stressed, rupture of the mechanically weakened surface layer around naturally occurring flaws will expose unaffected rubber and the process continues, resulting in cracking. These cracks can significantly weaken the rubber structure, which will cause failure of rubber components in certain applications.

That O_3 cracks rubber under stress has been known for a considerable time. A widely used method of protecting rubber is to introduce 'antiozonants' into the rubber blend, or to provide a protective outer coating, such as a wax. A comprehensive review of the ideal characteristics of antiozonants and the relative advantages and shortcomings of waxes as opposed to chemical antiozonants is given by Lewis (1986). In general, waxes are used where discoloration or staining needs to be avoided, where abrasion or severe stress is unlikely, where a surface bloom is acceptable and where a loss of adhesion is unimportant.

As far is understood, there is no 'threshold' of O_3 concentration for degradation of rubber. However, a sharp decrease in the ability of some antiozonants to raise the stress for crack initiation has been noted at very high (ppm) concentrations of O_3 (Braden and Gent 1962). However, it seems unlikely that this effect is operative under ambient O_3 concentrations.

An effect which may be significant for some components exposed to O_3 is the leaching effect of acidic water on antiozonants. For example, N - isopropyl - N' - phenyl - p - phenylenediamine, is added to tyre sidewalls but may be leached out by acidic water (Latos and Sparks 1969, John *et al* 1984). The consequences are dependent upon the exposure and construction of the component. For example, a tyre sidewall contains a sufficient reservoir of antiozonants such that it will not be depleted over the normal life-span of the product. However, physically thin products, such as windscreen wipers, may be affected so much that the life-span of the product is decreased. Thus the effect of leaching is an important economic consideration in situations where acidic rainfall may leach out antiozonants, thus forcing the manufacturer to increase the protection of the component and, therefore, adding to the costs.

Many rubber products are the result of assembly and vulcanisation of separately manufactured components. The adhesive properties of some rubbers are thought to be reduced by O_3. One study found that the adhesion of uncured rubber appeared to be related to O_3 exposure during storage and assembly and noted seasonal increases in failure of adhesion, which was attributed to variation in O_3 levels (Corish 1991).

There is little information available on the effects of O_3 on bulk polymers. Some chamber studies have been carried out (Brucksch 1967, Jellinick 1970, Jellinick 1974) in which O_3 was found to increase the rate of oxidation for some materials (polyethylene, polypropylene, Nylon and polystyrene). Lucki *et al* (1988) exposed polypropylene to high concentrations (2 $\mu g\ l^{-1}$) of O_3 for short periods and found embrittlement after 20 hours in the presence of UV radiation. At a concentration of 20 ppb, the exposure to receive this dose would be approximately 114 years. It would therefore be reasonable to conclude that embrittlement under the influence of O_3 at typical ambient urban levels is unlikely to be a problem. Lucki *et al* also noted that infra-red analysis showed detectable surface changes after 1 hour under these conditions but the significance of this is difficult to assess.

7.2.3 Surface Coatings and Ozone Damage

Surface coatings are defined here as materials which are applied to a substrate, forming a coherent film for protection and/or decoration of the substrate. Such materials include paints, varnishes and lacquers which are applied to wood, metal, stone, plastic and composite substrates. A paint film consists of a finely powdered opaque material (the pigment) dispersed in a polymeric material (the binder), with a refractive index of > 1.7. Powdered materials with lower refractive indices, when incorporated into surface coatings, are known as 'extenders'. Surface coatings are applied to materials with the binder dissolved in a suitable solvent which serves to reduce the viscosity and assist application.

There are few studies on the effects of O_3 on surface coatings. Of those that have been carried out, it is difficult to interpret the results, as surface coating technology has advanced rapidly in recent years and the experimental design of some of these earlier studies was flawed (Lee *et al* 1996).

Campbell *et al* (1974) exposed painted panels to 1000 ppb O_3 in a xenon arc accelerated weathering chamber for 1000 hours, some of which were shielded from UV radiation. The five paints were described as: oil house paint, latex coating (acrylic), industrial maintenance coating (alkyd), coil coating (urea alkyd) and automotive refinish (nitrocellulose/acrylic).

Degradation of the paints was equated with weight loss of material from the panels (Campbell *et al* 1974). If weight loss were simply due to erosion of binder and pigment from the coating, the results would be simple to interpret. However, the measurement is complicated by the leaching of water-soluble materials from the un-degraded coating and by the uptake of oxygen that accompanies the formation of oxygenated degradation products. Attenuated Total Reflectance infra-red spectroscopy (ATR) was also used to analyse the coating after exposure to 1000 ppb O_3 for 1000 hours. It was concluded that all the paints had suffered additional degradation in the presence of O_3, with the automotive refinish being the most degraded. However, the ATR method is not truly surface sensitive and measured the loss of binder relative to the amount of pigment present, rather than the absolute loss of material. Three of the 5 paints were also examined using scanning electron microscopy. The automotive refinish paint did not show any additional degradation due to the presence of O_3 (in conflict with the results from ATR) but the two building paints showed a detectable increase in surface degradation.

In another laboratory study, Spence *et al.* (1975) investigated the combined effects of ozone, sulphur dioxide, nitrogen dioxide and relative humidity on four paints: oil based house paint (linseed oil and soya alkyd), acrylic latex house paint, acrylic coil coating and vinyl coil coating. The painted panels were mounted on cooled racks (to enhance dew formation) and exposed to xenon radiation. High and low levels of the three pollutants and relative humidity were defined, and in the case of O_3, 80 and 500 ppb were selected, and the panels were exposed for 250, 500 and 1000 hours. Again, degradation was assessed by weight loss which was then converted to film thickness loss for the purposes of reporting. Weight loss was considered to be a more accurate measure of degradation than film thickness even though they recorded some weight gain (which was attributed to reaction with NO_2). The statistical treatment of the data did not appear to yield much information on the effect of O_3 other the observation that it was the only pollutant to have any measurable effect upon the acrylic coil coating.

There is evidence that works of art represent one specialist area of surface coatings where O_3 can produce degradation at relatively low atmospheric concentrations (Whitmore and Cass 1988, Whitmore *et al* 1987, Cass *et al* 1991) . The standards which have been discussed for museum environments are very low, e.g. 1-13 ppb (Cass *et al* 1991), on the basis that museum collections must be preserved for hundreds of years.

7.2.4 Textiles and Ozone Damage

Textiles may be conveniently divided into two categories: those used for clothing, and those used for other domestic and commercial purposes such as carpets, curtains, furniture coverings and possible outdoor uses such as tents and shop canopies. Most clothing is either kept or worn indoors for most of the time, where O_3 levels are lower than outdoors. Furthermore, the rate of wear and changes in fashion will mean that economic loss through air pollution damage at the consumer level is likely to be negligible. However, fabrics used in other applications such as carpets and curtains are expected to have longer lifespans than clothing.

Again, much of the research on the effects of O_3 on textiles is rather old. The main problem associated with O_3 is its effect upon dyes. In the 1960s, fading of nylon carpets occurred in warm humid areas of Texas and Florida and became known as 'Gulf-Coast fading'. Similar incidents were also reported in Los Angeles. Both Nylon 6 and Nylon 77 materials containing the dye Disperse Blue 3 were affected. Experiments which eliminated the action of sunlight identified O_3 at high (> 65%) relative humidities as the causative agent (Salvin 1969). Problems also occurred with polyester-cotton/permanent press fabrics stored in warehouses and retail outlets. In some cases, fading occurred on folds and edges of materials within a period of 10 days under ambient conditions. Again, O_3 was found to be the cause, where disperse dyes migrated to the permanent press finish and were subject to fading by O_3. Changes in the manufacturing process eliminated the problem but heavy economic loss was incurred at the time (USEPA 1978).

Other evidence suggests that dyed textiles may suffer visual degradation. In one study, fabrics were placed in light-sealed cabinets at a number of urban and rural locations in the USA. Two-thirds of the fabrics suffered fading and this was found to be significantly worse at the urban sites (Beloin 1972). However, the nature of the field study precluded the determination of the particular pollutant, or combination of pollutants, which caused the fading. In a follow-up laboratory study, fabrics were exposed to 0.5 and 0.05 ppm O_3 and it was found that visible fading occurred on one third of the sensitive fabrics at the lower levels of O_3 exposure and conditions of high humidity (90%) (Beloin 1973).

Decreases in tensile strength of textiles have also been observed. A 20% decrease in tensile strength of cotton was observed at O_3 exposures of 20 and 60 ppb in damp conditions (Bogaty *et al* 1952). The controlling factor appears to be the water content of the samples as no decreases in tensile strength occur in dry conditions (Morris 1966). Other weathering factors such as sunlight, heat, alternate wetting and drying are considered to be more important in the outdoor environment. The tensile strength of Nylon does not appear to be affected significantly by O_3 (Zeronian *et al* 1971).

7.2.5 Metals, Stone and Ozone Damage

Synergistic corrosive effects of O_3 in combination with S- and N- pollutants have been reported recently (Kucera 1996). The proposed mechanism for this is that O_3 increases the rate of oxidation of NO_x and SO_2 leading to enhanced formation of the strong acids, HNO_3 and H_2SO_4. The UNECE *International Cooperative Programme on Effects on Materials, including Historic and Cultural Monuments* (ICP) has now described exposure response functions for steel, zinc, copper, aluminium and bronze of the general form:

Change in mass = a + b[SO_2][O_3][time of wetness] + c,

where a and b are constants, and c is 'other factors' which may include rainfall acidity, time of wetness and chloride deposition.

In view of the indirect mechanism proposed for effects of O_3 on these metals, it is interesting that the UNECE (ICP) programme has yet to find an effect of O_3 on nickel, limestone or dolomitic sandstone. However, laboratory studies have found synergy between O_3 and SO_2 for effects on limestone, marble and travertine (Elfving *et al* 1994).

7.2.6 The Potential Costs of Damage to Materials by Ozone in the UK

The previous report of the group highlighted that no economic analyses of the costs of O_3 damage to materials had been made for the UK (PORG 1993). Indeed, the only costings that had been undertaken originated from the USA in the 1970s. Since the last report of the group, a scoping study has been undertaken to assess potential costs of damage in the UK (Lee *et al* 1996). This study revealed that these costs may be large, up to several hundred million pounds. However, as noted in the study, the basis upon which the estimates were made was very poor. The main constraints on a more reliable costing were lack of data on stock-at-risk and the virtual non-existence of damage functions.

Scaling the US estimate of damage by ozone to materials by population (excluding damage to textiles), correcting for inflation, resulted in an estimate of £345 million in current terms. Under the assumption that O_3 levels may well have been substantially higher in the USA in the early 1970s than in the UK at present, a weighting factor of 0.5 was introduced to give a range of £170-345 million for the UK. The problems associated with such a calculations are many: translation between currencies over such a time period is approximate at best, material usage may now be quite different, O_3 exposure is likely to be different, etc. In conclusion, the authors warned against using such an estimate, other than to indicate that current costs may be substantial.

An alternative approach of assessing the current stock-at-risk was made. For rubber, tyres represent approximately 50% of the market. Tyres, in common with many other natural-rubber based products, already have antiozonants in their formulation to prevent damage by cracking. The normal life-span of a tyre on a passenger vehicle is likely to be exceeded before damage occurs. However, commercial vehicle tyres have a longer life span as they may be re-treaded several times. Thus, cracking of the carcass may be an important factor. Although tyres constitute a large fraction of the rubber market, costs of O_3 damage to passenger vehicle tyres are expected to be small. Passenger vehicle tyres are expected to last longer in the future such that there may be an associated cost in increased protection (Lewis pers. comm.).

The incorporation of antiozonants into existing rubber formulations represents a real cost to the consumer. However, data on antiozonant sales and volumes produced are not readily available. Nevertheless, an independent estimate from the industry of cost of approximately £25 million has been made (Lewis pers. comm.). In the USA, the costs of antiozonants represent 57% of the costs to manufacturers, the other costs being associated with waxes and special polymer formulations (Stickney *et al* 1971). Under the assumption that the same scaling can be applied to the UK, the resultant protection costs to manufacturers are of the order of £60-70 million. A factor of 3 has been recommended to estimate retail costs (Stickney *et al* 1971), which would result in a cost to the consumer of the order of £200 million. This was not judged to be a satisfactory analysis because of the plethora of uncertainties and assumptions (Lee *et al* 1996), but again, it indicated that costs may be substantial.

The final economic analysis relates to surface coatings. Because of the dubious quality of previous experiments on O_3 and surface coatings, Lee *et al* (1996) could not use the results to generate damage functions. However, the results of previous work indicate that 'damage' may occur after 4-8 years exposure at 15 ppb O_3. Using other data on stock at risk and extrapolating to the UK and repainting costs, an annual estimate of £60 million was associated with a 5 ppb increase in O_3 (Lee *et al* 1996). The uncertainties in this calculation, are, once more, large. If the damage recorded by Campbell *et al* (1974) and Spence *et al* (1975) was only slight, it could be concluded that O_3 is unlikely to affect the service lifetime of surface coatings significantly. If this is correct, associated costs will be negligible.

It is evident that substantial economic loss was incurred in the United States in the 1960s through O_3 damage of textiles. Manufacturing processes have changed in order to eliminate the problems and it is considered that any preventative costs associated with O_3 damage are now lost within the overall manufacturing process. We therefore conclude that the textile industry would be unlikely to respond to a reduction in O_3 concentrations from the current levels, and hence for the purposes of developing policy, the associated costs are negligible.

No attempt has yet been made to assess the costs of O_3 damage to metals, following the recent development of appropriate exposure response functions from the UNECE ICP.

Overall, therefore, it is concluded that the costs associated with the exposure of materials to O_3 could be of the order of a few hundred million pounds per year. However, at the present time there are regrettably few data available with which to confirm this. Particular uncertainty surrounds the marginal costs of a change in O_3 concentrations. Measures taken to mitigate against O_3 effects may be so embedded within manufacturing processes and culture that they do not respond to a regional change in ozone levels.

7.2.7 Exposure of Materials in the UK to Ozone

Measurements of O_3 levels have been mostly made in rural areas of the UK, where they are generally much higher than urban levels, because of the high source strength of NO, the main atmospheric sink for O_3, in urban areas.

The concept of a critical load, or critical level is not appropriate to materials as a threshold level, above which unacceptable damage occurs is implied. Materials, in general, deteriorate under natural conditions in the absence of atmospheric pollutants. Furthermore, damage tends to be additive and non-reversible. Thus the concept of an acceptable rate of degradation is more appropriate. Such a rate may be useful in combination with damage functions. An alternative definition is an acceptable lifetime. Defining an acceptable rate of degradation, or lifetime, is more problematic than a critical load or level.

The definition by analysts of an acceptable rate of degradation, particularly for fine art materials, appears rather presumptive. 'Acceptability' is a political issue and should thus be defined by policy makers; for the time being it is probably better that analysts aim to present policy makers with an assessment of effects under different scenarios. This will be made easier once the costs associated with O_3 exposure can be characterised with reasonable accuracy, so that the 'rate of degradation' can be presented in a more easily understood manner.

The issue is complicated by the apparent synergy between pollutants, particularly O_3 and SO_2 (Kucera 1996). Definition of a critical level in terms of the product of SO_2 and O_3 may therefore be more appropriate than assessment of a critical level for either pollutant alone.

In comparison to critical loads, such concepts are in their infancy, and much more work remains to be done on refining the concept for its use as a policy tool. The last such workshop, under the auspices of the UNECE (1993), was held in 1993 and although this concept was discussed, little further progress has been made. As we reported previously, an acceptable rate of deterioration of 20 ppb of O_3 was set at this workshop.

At present there is little evidence not to assume that effects on materials are linear or additive. Thus the most appropriate statistic on O_3 levels is a mean concentration over a given period, as it gives a quantitative measure of exposure (concentration time).

Mean levels of O_3 from some of the UK's automatic urban network sites are given in Appendix 4.1. One of the problems associated with assessing the extent of effects, if such means were available, is the lack of data on the fine spatial variability of O_3 levels in urban areas. If such an urban effect is present, it is likely to the result of localised 'hot spots' of its main atmospheric sink, NO, rather than locally enhanced levels.

Figure 7.21 shows mean O_3 levels over the UK, as mapped by the procedures described in Chapter 3 and Appendix 4.2. This map reveals that levels of 20 ppb are exceeded over 82% of the UK land mass. Of this area, *ca* 2% is urban which represents 36% of the total urban land area.

Thus, based upon these data and such a level of 20 ppb, 'unacceptable' rates of damage to materials might be expected across much of the urban areas of the UK. However, this interpretation should not be taken too far until a better basis for selection of such a level is achieved.

7.2.8 An Approach to Determining Ozone Damage to Materials in the UK and Preliminary Results

The concern over materials damage in the UK is driven by two factors: the previously unquantified scale of the economic impacts, which may be significant, and the potential rise in urban O_3 levels discussed in Chapter 9. Given that 85% of the UK population live in urban areas, the likelihood is that the population's material goods are also found generally in urban areas.

A research programme has been initiated by the Department of the Environment, Transport and the Regions involving several groups: AEA Technology, the Institute of Terrestrial Ecology, the Paint Research Association, the Malaysian Rubber Producers' Research Association and the Meteorological Office.

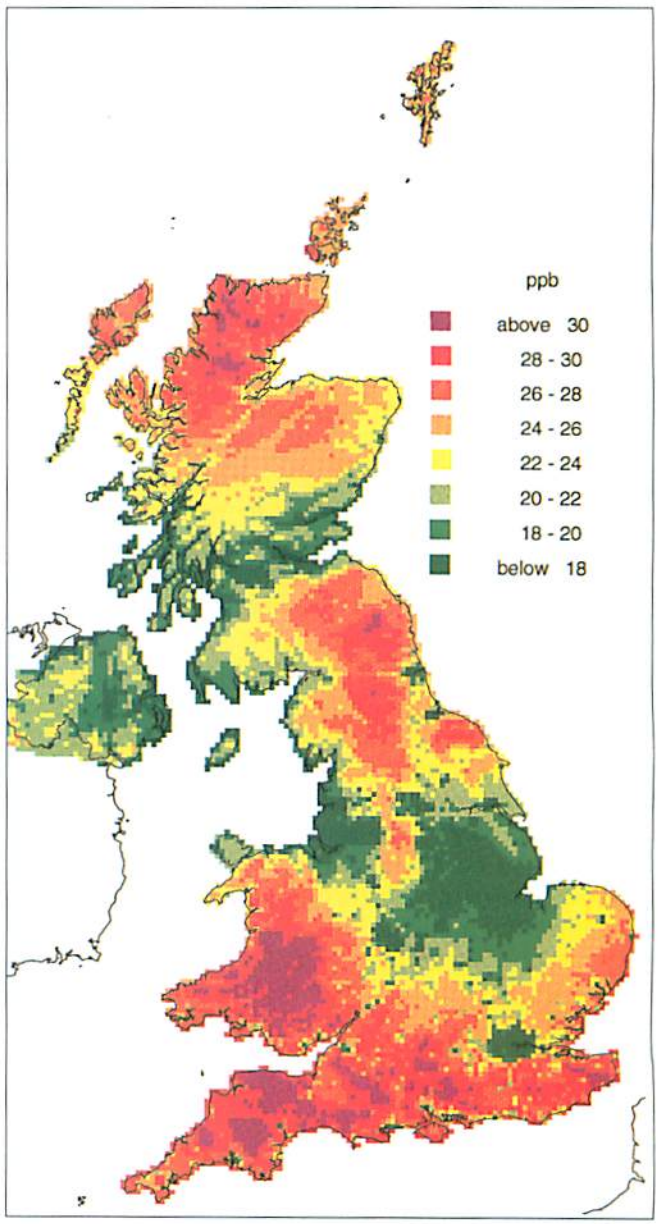


Figure 7.21 Annual mean ozone concentration (ppb) in the UK, 1990-94 rural mean compensated for urban areas, see Appendix 4.

The programme is designed to follow an 'impact pathway' approach, whereby an attempt is made to identify all the stages between emission and damage, and associated costs, so that a scenario analysis may be performed. An example of this approach is shown in Figure 7.22 for polymeric materials. The two major constraints of lack of damage functions and data on stock at risk are both being addressed. The first phase of the programme consists of an initial analysis of the stock-at risk followed by laboratory exposure at high levels of O_3 to determine the relative sensitivity of products.

A UK inventory for buildings, paint and repair costs has been compiled, along with vehicle type. Work underway includes re-assessing the anti-ozonant market, establishing product life-times and costs for replacing rubber goods.

It is not enough to identify those products at risk, it is also necessary to identify whether those sensitive products are of economic significance per se, or may be so in the event of premature failure.

Two examples of the costs of component failure may be considered: a windscreen wiper blade is relatively sensitive as it is only in occasional use, it is a product in widespread use and is susceptible to leaching of its protective antiozonants by exposure to acidic water and its thin physical structure. However, replacement and failure costs are negligible. A second example, a passenger vehicle constant velocity joint boot, is similarly widespread in its use, is of a similar cost to a pair of wiper blades, but the costs associated with its undetected failure and subsequent replacement may be of the order of 25 times its replacement value due to potential failure of the bearing that it serves to protect.

These examples illustrate the complexity of providing an economic analysis of damage to materials, from any cause. Given that failure of other materials are likely to result from exacerbating factors in the ordinary exposure of them to the outdoor environment, extrapolation of laboratory analyses are difficult.

In order to overcome some of these difficulties, materials are first being exposed in laboratory chambers at very high concentrations (> 1 ppm) in order to determine the most vulnerable types, and then in 'open top chambers'. Open-top chambers have been used extensively in the past to provide exposure of vegetation to controlled levels of gaseous pollutants whilst maintaining realistic conditions of temperature, UV radiation, humidity, etc. Several chambers are linked to an O_3 monitor and an O_3 generator. In order to provide greater exposure, yet simulating the real dynamics of outdoor exposure, a computer tracks the ambient conditions and controls the output of the O_3 generator to deliver multiples of ambient O_3 by factors up to x4.

Various paints and rubbers have been placed in the open-top chambers, as a result of the laboratory experiments. Natural rubbers protected with different levels of antiozonants have been exposed, along with polychloroprene rubbers. Cracking of the rubbers has been observed, consistent with the differing levels of exposure, although detailed analyses are not yet available. In parallel with these experiments, natural rubber compounds have been exposed at UK urban and rural O_3 measurement sites. The purpose of this was to determine that cracking was, indeed, a result of O_3, and not other pollutants. The results indicate that the crack-rate is consistent with the O_3 dose to the rubbers. However, one of the more surprising results is that rubbers exposed to light, appear to 'condition' and that O_3 cracking is greatly reduced, even in rubbers with carbon black. It is thought that this is related to photo-oxidation from UV. Preliminary analysis of some products, e.g. latex rubber gloves and self-adhesive envelopes reveal substantial deterioration of lifetime and functionality from higher doses in the open-top chambers.

The tests to paints and surface coatings include: colour change; gloss; flexibility; water resistance; solvent resistance. Initial results indicate that wood paints and some blue colours of automotive paints are the most vulnerable in terms of colour changes. Both positive and negative changes in flexibility were noted, possibly as a result of degradation of substrate resins. No results were yet available from the open-top chamber systems as exposure times were required to be much longer than those in the laboratory.

Atmospheric modelling of the horizontal and vertical profiles of O_3 has been undertaken at the Meteorological Office. An initial model of London has been built using 1 km resolution emission inventory data. The results show very strong vertical gradients of O_3, as a result of strong NO injection into the lower layers, emphasising the need to consider vertical resolution in the materials inventory. Future scenarios will be modelled to determine possible changes in material exposure to O_3, and the largest changes (as a result of the increase in usage of 3-way catalysts on cars) are expected in the lowest 20 m.

7.2.9 Conclusions

- Whilst the phenomenon of rubber cracking is well known, exposure-response functions are not available. Most of the bulk use of rubber is associated with passenger tyres which normally wear out before damage from O_3. Other rubber components may have small value but high associated replacement and/or failure costs. The existing cost of antiozonants is estimated to be of the order of £25-200 million to the consumer. If urban O_3 levels were to rise, it is not currently known whether increased protection from antiozonants would be required.
- The impact of O_3 on surface coatings is understood poorly. Previous experiments have identified changes in surface properties, but results are conflicting and there were serious deficiencies in experimental design and interpretation of the results. Re-painting costs are likely to be much higher than the cost of materials, but an 'acceptable lifetime' is difficult to define and is likely to be highly subjective. Other influences on surface coatings are also likely to be significant. Potential costs associated with a 5 ppb increase in urban O_3 have been estimated to be in the range of £0-60 million.

- Fading of textiles because of O_3 exposure does not seem to be a problem now. Given that the use of fabrics in the outdoor environment is limited, it is likely that economic loss because of damage to the tensile properties of fabrics by O_3 is minimal. It is therefore concluded from the limited available evidence, that economic loss from O_3 damage to textiles is probably negligible. It should, however, be noted that some textiles in museum collections may fade from O_3 exposure (Whitmore *et al* 1987). This damage, however, is difficult to assess economically.
- The economic analyses reported here are very uncertain but indicate that the potential overall costs of O_3 effects on materials could be of the order of several £100 million. These costs may rise, should urban O_3 levels increase.
- Preliminary results of a research project have confirmed, experimentally, that further degradation of both natural and protected rubber compounds was detectable for changes in O_3 concentrations by a factor of 2. Certain protective coatings for wood and vehicles show measurable changes in colour upon exposure to O_3. Modelling of the vertical profile of O_3 in urban areas indicates very strong gradients, which may change upon reductions of NO concentrations from emission control measures.

7.3 The Effects of Ozone on Human Health

A detailed account of the effects of ozone on man was provided in the Third PORG Report (PORG, 1993). This dealt with mechanisms of effect and the responses recorded in chamber studies of ozone. Epidemiological studies of ozone were also briefly reviewed. This section updates the contribution provided in 1993. For the first time, this group presents an estimate of exposure to ozone over the UK. Also the new approach adopted by WHO as a result of advice provided by an

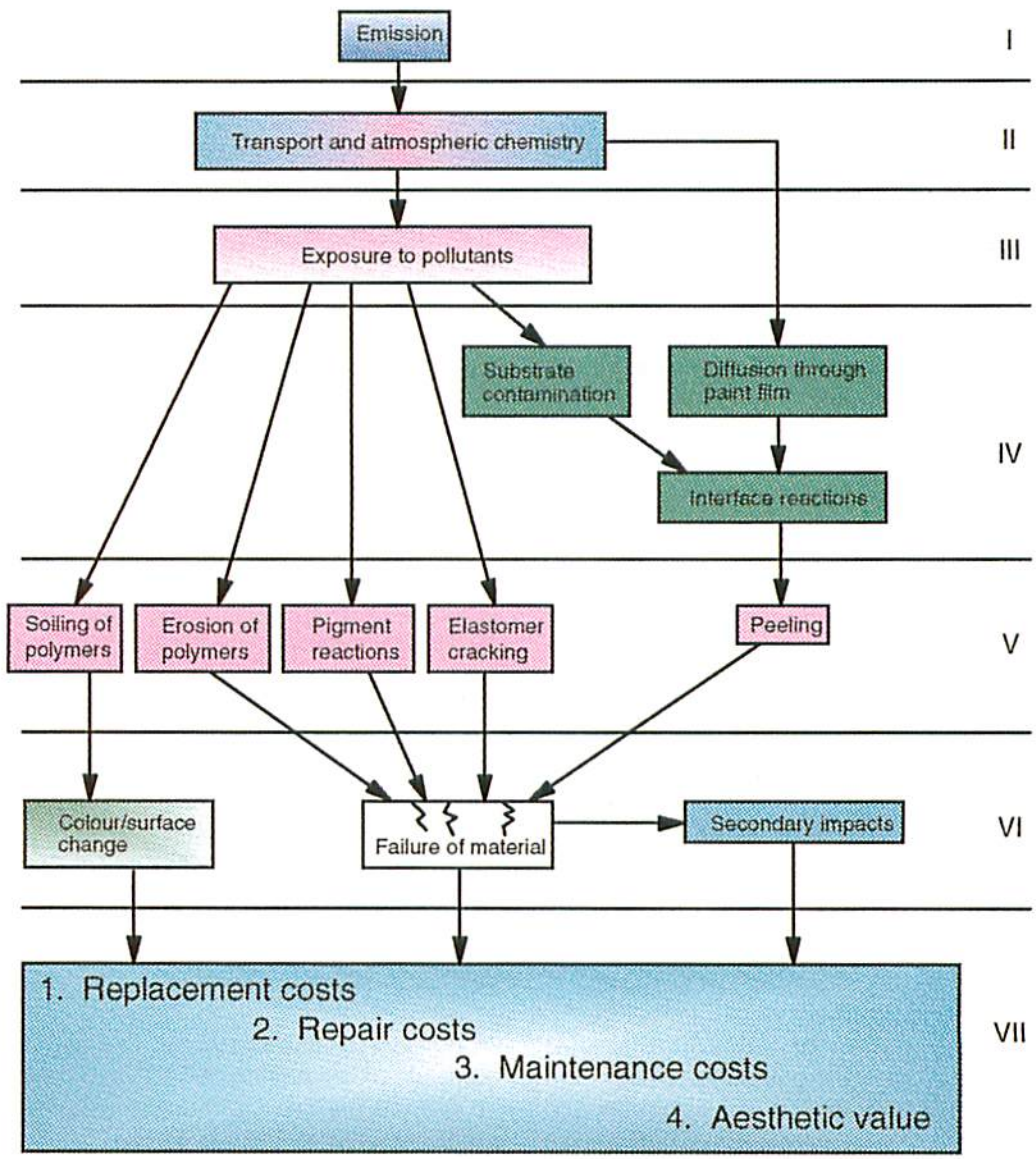


Figure 7.22 Example of an impact pathway for the effects of atmospheric pollution on polymeric materials. The term 'secondary impacts' refers to effects such as rotting window frames that may arise from the ingress of water following failure of polymeric sealants. The costs associated with secondary impacts should probably be attributed to poor maintenance rather than pollution in most cases.

Expert Group which met in October 1994 is outlined (WHO, 1995). This Group advised revision of the Air Quality Guideline for ozone and contributed an exposure-response curve for effects on health at concentrations above the Guideline. In addition, recent studies by Professor R. Anderson of the effects of ozone on hospital admissions in the UK have been used to make preliminary estimates of the effects of ozone on public health in the UK. This initial work will be provided to an expert group convened by the Department of Health to quantify risks to health from air pollutants.

7.3.1 Biochemical and Cellular Effects of Ozone

No fundamental shift in our understanding of the mechanism of action of ozone has occurred. Ozone is a reactive gas and the most irritant of the common air pollutants (Bates, 1995). At low and commonly occurring concentrations, it has been shown to induce an inflammatory response in the lung. Lavage studies in both man and animals have provided details of this response. It is clear that the inflammatory response may occur even when no changes in conventional physiological indices of lung function are recorded (Basha *et al* 1994).

On penetration into the respiratory system ozone reacts vigorously with a wide range of organic molecules. Ozone is such a reactive molecule that it is unable to penetrate for any distance through a system containing lipids and proteins and other organic molecules, without undergoing reaction. This process is described as reactive absorption. Studies have demonstrated that ozone is unlikely to penetrate more than 1 micron across the liquid lining of the airways. (Pryor, 1992). Of the molecules with which ozone reacts some, like glutathione and uric acid, provide a defensive system which reacts with and removes inhaled ozone. The distribution of these antioxidant molecules in the respiratory tract has been studied and it is now thought that uric acid provides the major defense in the nose whilst glutathione is dominant in the lower respiratory tract.

The mechanisms of secretion of uric acid and glutathione are not known in detail but are clearly capable of responding to a reduction in surface concentrations of antioxidant. A considerable inter-subject range of concentrations of uric acid has been demonstrated in the nose. Women seem to have rather lower concentrations than men and some women seem to produce very little uric acid (Housley *et al,* 1995). Whether this has implications for individual sensitivity to ozone remains unknown. There is some preliminary evidence to suggest that the secretion of antioxidants is stimulated by exposure to ozone (Holgate, 1995). The increase in production of antioxidants after exposure to ozone provides a plausible explanation for the phenomenon of tolerance: a reduced response to ozone over a series of daily exposures. There is less evidence to show that the inflammatory response decreases with repeated exposure than there is regarding the response measured in terms of indices of lung function. It is also possible that tolerance should be interpreted not as an improvement in defence but as the development of an inability to respond. The implications of the latter are much more worrying than those of the first suggestion (Dept. of Health, 1991). Exposure to high ambient concentrations of ozone does not, however, remove the capacity to respond to day to day variations in concentration. Whether this indicates a resetting of the threshold of response is not known. Further work to resolve the phenomenon of tolerance is urgently needed.

Reactions with other molecules including lipids leads to the generation of free radicals. A cascade of free radical mediated reactions follows and the inflammatory sequence is set in motion. The involvement of a range of inflammatory mediators including interleukins IL-1, IL-6, IL-8, TNF-α PGE_2 and ICAM molecules has been repeatedly demonstrated in animals and man (Dept. of Health, 1991). There is evidence to suggest that a greater and longer lasting response is called forth in asthmatic individuals though this does not seem to be reflected in changes in indices of lung function.

The inflammatory response is characterised by migration of polymorphonuclear leukocytes from the blood into the interstitial tissues and the movement of these cells into the lining fluid of the airways. As in all inflammatory responses an increase in capillary permeability occurs and plasma proteins leak across capillary walls. These also leak across the epithelial barrier into the lining fluid of the airways. This implies that some weakening of the intercellular junctions of the epithelial cells occurs. It is likely that the tight junctions located high on the sides of the columnar epithelial cells are affected.

Ozone penetrates deeply into the lung and modelling studies have shown that the peak absorption may occur at the terminal bronchiole and in the proximal acinus (Miller *et al,* 1978). In this region of the respiratory tract goblet cells are few and Clara cells provide the bulk of the antioxidant molecules of the liquid lining of the airways (Komaromy & Tigyi, 1988). Damage to Clara cells by ozone has been described.

Long term exposure to ozone leads, in animal models to damage of the respiratory bronchioles, though these are not well developed in laboratory rodents, and to the alveolar ducts. This process is described as bronchiolarisation of the alveolar ducts and the epithelium comes to resemble closely that of the terminal bronchioles (Hyde *et al,* 1989). If damage is maintained by long term exposure, fibrosis follows. Resolution of established ozone induced fibrosis has not been studied.

A number of authors have suggested that ozone is capable of increasing the prevalence of lung tumours in animals exposed to recognised pulmonary carcinogens. Opinion on this is divided : some studies have produced clear negative results and others, positive results (Witschi, 1988). The general perception that the increase in risk of lung cancer resulting from exposure to ambient levels of ozone is negligible seems not to have changed over the past few years.

7.3.2 Controlled Chamber Studies with Ozone

Extensive studies of the changes in indices of lung function produced by exposure to ozone have been undertaken (Dept. of Health, 1991). In recent years spirometric studies have been combined with bronchoalveolar lavage (BAL) and the monitoring of inflammatory mediators and counts of inflammatory cells. The results of the latter type of study have been considered above.

It has been demonstrated that about 50% of inhaled ozone is absorbed in the upper respiratory tract and does not reach the trachea. The percentage so absorbed is reduced during mouth breathing as occurs during vigorous exercise.

Efforts have been made to define a threshold of effect of ozone in both normal and asthmatic subjects. In both, statistically significant changes in FEV_1 (forced expiry volume) have been recorded on exposure to 80 ppb ozone for 6 hours and to 100-120 ppb ozone for 1-2 hours (Hazucha, 1987). Studies vary a little in terms of the exposure regimen involved and this may account for the small variations in the results. A few studies have shown that asthmatics are more sensitive to ozone than other individuals though the difference was not great and is of questionable clinical significance (Ball *et al*, 1993). It has been shown that changes in BAL levels of IL-6, IL-8 and neutrophils occurred in asthmatics on exposure to ozone at a concentration which did not produce this response in normal controls (Williams *et al*, 1992; McBride, *et al* 1994). This study involved short term exposure to 300 ppb ozone and its relevance to the effects of ambient exposure is uncertain.

Detailed studies of the dose response relationship for ozone have been conducted by Larsen (Larsen *et al*, 1991). Both the concentration of ozone and the duration of exposure were shown to be important in defining the response in terms of a decrement of FEV_1. Concentration appeared to be more important than duration of exposure. Taking z as the number of standard deviations that an FEV_1 percentage decrease is located away from a 50% decrease, the regression equation which describes the relationship is:

$$z = -0.175 + 0.911\ln(t.C^{1.320})$$

For a 5% reduction in FEV_1 $t.C^{1.320} = 0.20$.
For an eight hour exposure C = 61 ppb

Responses as small as a 5% change in FEV_1 have been seen as clinically insignificant. There is, however, a wide inter-subject range in response and a number of studies have shown that this variation in response is maintained amongst asthmatic individuals who may under normal conditions have impaired lung function. Shifts in the population distribution curve of lung function may lead to a significant increase in the number of subjects being in the "at risk" group.

An important area of study has been of the effect of exposure to ozone on the response to allergen amongst sensitised individuals. A number of studies have shown that pre-exposure to ozone enhances the response to allergen (Molfino *et al*, 1991; Jörres *et al*, 1994). The concentrations required to produce this effect commonly occur under ambient conditions.

7.3.3 Effects of Ozone on Public Health

As with other air pollutants it has proved difficult to design studies which allow examination of the effects of ozone alone. Ozone concentrations tend to be highest during the summer months and to be associated with raised levels of other photochemically generated pollutants including acid aerosols. The perception that the latter may play an important part has grown and recent studies have shown that on high pollution days the effects of acid aerosols may dominate the overall response. A number of important groups of studies have been reported in recent years.

7.3.3.1 Summer Camp and other Panel Studies

A series of studies conducted in the US have demonstrated a relationship between indices of lung function, FEV_1 and PEFR and ambient concentrations of ozone (Lioy *et al*, 1985; Spektor, Lioy, *et al*, 1988). These studies have involved both healthy and asthmatic children who have been exposed whilst exercising for long periods out of doors each day. In many of these studies individual regressions of change in FEV_1 on ozone concentration have been calculated and the distribution of the slopes examined. Consistent results have been obtained with decrements of FEV_1 of the order of 0.3-0.8 ml/ppb ozone. In adults the decrement is about 2 ml/ppb ozone which allowing for the larger adult lung is similar to the figure for children. A considerable subject to subject variation in response was noted with some children losing 1.5 ml of FEV_1 per ppb ozone. In studies of young adults this variation in response has also been noted. Spektor reported that of 30 adult subjects exposed to 120 ppb ozone for one hour whilst exercising, 7 sustained reductions in FEV_{25-75} of 26% or more from the baseline (Spektor, Lippmann *et al*, 1988). This is a substantial change and in someone with already depressed lung function would be clinically significant.

Studies in panels of school children in The Netherlands have revealed a relationship between daily ozone concentration and indices of lung function (Hoek, Brunekreef *et al*, 1993; Hoek, Fischer *et al*, 1993). In some studies the effect has been most marked when ozone concentration lagged by a day or two has been regressed against indices of lung function. In these studies careful adjustment for confounding by temperature and other pollutants has been made. In general these studies have revealed smaller effects than the summer camp studies in the US. This may be due to the lower exercise levels in school children and the lower time spent out of doors. In some studies no relationship between ambient concentrations of ozone and lung function were found. In studies involving cyclists exercising vigorously a relationship between lung function and ozone was regularly found (Brunekreef *et al*, 1994).

Attempts have been made to discover whether those suffering from asthma represent a sensitive sub-group of the population with regard to the effects of ozone. Requirement for treatment including visits to hospital

emergency departments amongst asthmatic children have been shown to be related to ambient ozone concentrations (Cody *et al*, 1992) though other studies have failed to demonstrate an effect (Rennick & Jarman, 1992). Whether asthmatic children sustain greater loses of FEV_1 as a result of exposure to ozone remains unclear.

7.3.3.2 Cross Sectional Studies

It has been suggested that those who live in areas where higher concentrations of ozone occur are:

- more likely to suffer from asthma;
- likely to have generally depressed lung function,

in comparison with those who live in low ozone areas (Schmitzberger *et al*, 1992). A number of studies have examined and generally confirmed this hypothesis. It has been found that military recruits from areas of high background concentrations of ozone have generally poorer lung function than those from areas where levels of ozone are low (Ito *et al*, 1993). These studies have confirmed the findings reported by Schwartz in 1989 which showed that lung function was inversely related to ambient ozone concentration at concentrations in excess of 40 ppb (annual average concentration) (Schwartz, 1989).

Studies designed to look at the relationship between the prevalence of asthma and other chronic respiratory diseases and long term concentrations of ozone have produced mixed results (Abbey *et al*, 1993; Detels *et al*, 1981). In some studies it has proved difficult to distinguish between possible effects of ozone and those of particulate matter. In the COMEAP report on Asthma and Outdoor Air Pollution it was concluded that whilst there was some evidence to support the suggestion that the prevalence of asthma was related to ambient levels of pollution (studies from California) it was unlikely that the effect in the UK would be large.

A number of studies of the relationship between hospital admissions and admissions to hospital for respiratory diseases have demonstrated an effect of ozone (Thurston *et al*, 1992). This has been clearest perhaps, in studies from Eastern Canada where the combination of ozone and acid aerosols has a clear effect on admissions for asthma (Bates & Sizto, 1983). These studies have in general taken account of the known effects of confounding factors such as temperature.

7.3.4 Estimates of Ozone Exposure in the UK

7.3.4.1 Introduction

In making estimates of the impacts on health of ozone, and other pollutants, on a national scale, the definition of concentration patterns over the UK and an assessment of exposures has been a particular problem. Although a detailed assessment of personal exposures to ozone is still unavailable, considerable advances have been made since the previous reports of PORG in mapping ozone concentrations over the UK.

This section presents results of some recent work by Stedman and colleagues on mapping 8-hour ozone concentrations in 5 km x 5 km grid squares over Great Britain. It is then a relatively straight forward mechanical step to multiply these concentrations by coefficients derived from published epidemiological studies relating ozone concentrations to health-related outcomes such as hospital admissions. However there are issues of interpretation and assessment of the health-effect studies which are required before definitive conclusions can be drawn, and these go beyond the role of PORG. During the period of preparation of this report a sub-group of the Department of Health's Committee on the Medical Effects of Air Pollutants was set up, to attempt to quantify the risks to health in the UK from a series of pollutants, including ozone. The work of this sub-group on ozone will rely heavily on the exposure assessments presented here, and will use similar techniques for other pollutants.

7.3.4.2 Ozone Mapping

The air pollution measurement data used in this study were taken from the UK Department of the Environment Automatic Monitoring Networks (Bower *et al*, 1996). Hourly ozone concentration measurements for the summer of 1993 (April to September inclusive) were available from 15 sites within the Automatic Rural Monitoring Network (ARN) and 11 sites within the Automatic Urban Monitoring Network (AUN). Measurements for the summer of 1995 were available from 5 ARN and 16 AUN sites. The ARN sites are generally in open country locations, in areas of low population density, well away from major roads and industrial areas. The majority of the AUN sites are in city centre locations. Ozone concentrations at roadside locations are often significantly reduced due to the close proximity to NO emissions from road traffic. All of the sites used in the study are away from the roadside since roadside sites are generally only representative of a very restricted area.

The mapping procedure, which required calculation of maps of estimates of concentrations in both rural and urban areas, involved several steps:

The maximum of running 8-hour average ozone concentration was calculated for each site for each day and a map of rural ozone concentrations was calculated by interpolation from measurements at rural sites (an example is shown in Figure 7.24B). The daily maximum of running 8-hour average ozone concentrations in urban areas tends to be different from the grid square value interpolated from rural measurements. This is because the NO present in urban areas (a large proportion of which is emitted from vehicles) reacts with ozone to produce NO_2, reducing the ambient ozone concentration (Chapter 3 and PORG, 1993). The impact of NO emissions on ozone concentrations during photochemical episodes is not constant and varies from city to city due to the different NO emission intensities and from day to day according to meteorological conditions.

Ozone measurements are available in a number of urban areas for the summers of 1993 and 1995. These can be compared with the interpolated rural ozone values and an urban influence, UI, can be defined as:

$$UI = \frac{\text{rural interpolated ozone - urban measured ozone}}{\text{rural interpolated ozone}}$$

UI will have a value of 0 for a rural site and a value of 1 for an urban area where the measured ozone value was zero. It is not possible to measure ozone concentrations in all 5 km x 5 km grid squares and hence to calculate the UI for each square directly from measurements. Values of UI for each day for each urban area in the country must therefore be estimated before a map of ozone concentrations can be calculated.

It is reasonable to assume that for a constant NO emission intensity UI will remain constant on a particular day across distances of several tens of km for which the meteorology should be consistent. If a linear relationship between UI and an indicator of NO emission intensity is assumed (for constant meteorology), then strength of urban influence factor 'a' can be calculated for each urban monitoring site for each day.

$$UI = a \times urblc$$

where urblc is the proportion of land cover that is defined as urban or suburban within the 'Land Cover Map of Great Britain' (Fuller *et al* 1994). The NO emission intensity will depend to a large extent, on the amount of traffic activity in a given area, which will tend to be linearly related to the proportion of 'urban + suburban' land cover. Land cover information has been used in preference to published NO_x emission inventories, which are currently only available for the UK at a grid resolution of 10 km x 10 km (Salway *et al* 1996).

The strength of urban influence factor a, will not necessarily be constant across the country on a particular day due to variations in meteorology over distances greater than several tens of km. An interpolated map of a was therefore calculated for each day and combined with the land cover information to calculate a map of UI for each day. A map of daily maximum of running 8-hour average ozone concentration in urban and rural areas was then calculated from the rural interpolated ozone map and the map of UI:

Estimated ozone = UI x rural interpolated ozone

and an example is shown in Figure 7.24A.

7.3.4.3 Preliminary Estimates of Health Effects

In assessing the effects of air pollutants on a national scale, a major difficulty has up until now been to make even an approximate assessment of exposure across the country. The calculations outlined in the previous section represent an important advance in achieving this for ozone (and similar techniques are being applied for other pollutants). Having done this, it is a relatively straightforward task, in principle, to then take coefficients from epidemiological studies relating health outcomes to ozone concentrations and obtain an estimate of the magnitude of the particular health outcome on a national basis.

There are, however, issues relating to the interpretation of the health effect studies which go beyond the remit of PORG. The Department of Health has set up a sub-group of the Committee on the Medical Effects of Air Pollutants (COMEAP) to attempt to quantify the risks to health from air pollutants, and this group will take further the initial work summarised here, and publish its findings in 1997. In the interim, an outline of the method of estimating health effects is given below, using hospital admissions for respiratory disorders as an example.

7.3.4.4 Relative Risk Coefficients and Thresholds of Effect

There are several sources of recently published coefficients relating to hospital admissions to ozone concentrations. Ponce de Leon *et al* (1996) examined the relationship between daily emergency admissions for lower respiratory diseases and fixed 8-hour mean ozone concentrations in London over the period April 1987 to February 1992 and reported a single combined coefficient of 0.00163 for the coefficient for the log of hospital admissions per ppb of ozone (with 95% confidence intervals 0.00083, 0.00242).

While the above study is the only one available for the UK, the World Health Organisation has recently summarised a large number of studies from North America as well as Europe and presented exposure-response relationships. The coefficient for hospital admissions for respiratory disorders given in the WHO summary is 0.003810 ppb^{-1} O_3.

A further source of uncertainty, and one which is potentially larger than uncertainties over the coefficients, concerns the question of whether or not to use a threshold of effect in estimating the health impact of ozone. Ponce de Leon *et al* (1996) found indications of a threshold value for fixed 8-hour mean in ozone in London in the range of 40-50 ppb. On the other hand, the advice from the WHO panel who considered ozone was that in using the linear exposure-response relationship mentioned above, no threshold should be assumed.

Accordingly, in this preliminary estimate, calculations are presented using no threshold and a threshold of 50 ppb 8-hour mean.

7.3.4.5 Hospital Admission Estimates

An estimate of 34.5 admissions per 10,000 people for the expected rate of hospital admissions for respiratory disorders for this study was provided by the Lung and Asthma Information Agency, which holds Hospital Episode data for respiratory diseases for England, and represents the average over English Health Authorities for the six month period April to September 1993. The rate of admission per 10,000 varied from 26.4 for the lowest Regional Health Authority to 46.4 for the highest. This is an estimate of the range of likely admission rates. The number of admissions per 10,000 per day can then be calculated by dividing the rate for the six month period by the number of days that this represents. This estimate was used in the calculations of estimates of additional hospital admissions due to ozone episodes for the summers of 1993 and 1995.

The total population potentially at risk in England in June 1993 was 48,532,700 and the total number of respiratory admissions for the summer of 1993 was 167,340.

Table 7.4 The number of the additional hospital admissions for respiratory disorders, calculated with different mapping methods.

Admissions	maps as used	a = 0.0	a = 0.5	a = 1.0
23/05/93	9.4	19.5	7.2	6.6
24/05/93	9.3	26.0	8.2	7.5
06/06/93	22.4	25.8	2.7	2.3
08/06/93	25.2	43.4	5.7	5.0
09/06/93	33.0	64.8	30.6	29.0
10/06/93	10.3	26.8	11.7	10.9
Total	**109.5**	**206.4**	**66.2**	**61.3**

The total population of GB represented by the 5 km x 5 km grid square map of population from the 1981 census used in this study was 53,341,200. Assuming that the rate of respiratory admissions in Wales and Scotland is similar to the rate in England, the total number of respiratory admissions for the summer of 1993 for GB can therefore be estimated to have been 183,920.

The relative risk of hospital admissions for respiratory disorders for each day and each grid square was calculated if the mapped ozone concentration was

relative risk = exp((ozone-T) x 0.001638)

where T is the threshold, either 0 or 50 ppb.

The percentage increase in hospital admissions (the additional risk) can therefore be calculated as 100 x (relative risk - 1). The number of additional hospital admissions for respiratory disorders due to ozone for each grid square for each day was then calculated from the relative risk for each square, population census data and an estimate of the expected average number of hospital admissions for respiratory disorders for England for the summer months. The total number of additional admissions for each day attributable to ozone were then summed from the admissions in each individual grid square and these daily totals were summed to provide an estimate of the total number of additional admissions for the whole summer.

7.3.4.6 Results

Using the relative risk coefficients derived from the UK study of Ponce de Leon *et al* (1996) for 1993 and 1995 assuming a threshold of 50 ppb, the estimated hospital admissions are 184 and 643 respectively. This represents a relatively large interannual variation, of about a factor of 3. However the threshold assumption exerts a much larger influence on the estimation. For 1995, assuming no threshold, the estimated hospital admissions are 11195 over an order of magnitude greater than the result obtained by assuming a threshold of 50 ppb. In the summer of 1995 this represents a range of 0.35% to 6.1% of total hospital admissions for respiratory disorders. This issue will be considered further by the COMEAP sub-group referred to above.

The effects of ozone on hospital admissions are only one of the reflections of the effects of ozone on health. It is likely that on days when concentrations of ozone are raised and an increase in admissions to hospital occurs, some individuals will experience symptoms. These may include some shortness of breath, discomfort on breathing deeply and a decline in competitive athletic performance. On days when concentrations of ozone are unusually high eye irritation may occur.

7.3.4.7 Uncertainties

The 95% confidence limits of the coefficients of Ponce de Leon *et al* (1996) give the range of 93 to 276 (0.051% to 0.150% of total admissions) number of additional hospital admissions (for 1993) for the best estimate of the 34.5 hospital admission rate and 50 ppb threshold. Taking the highest and lowest coefficients and the highest and lowest hospital admissions rates, gives additional admissions in the range 71 to 372 (0.039% to 0.202%) for the 50 ppb threshold. The number of additional admissions is higher if the WHO (1995) risk coefficient and a threshold of 50 ppb are used, 441 admissions represents 0.240% of the total admissions. Interestingly, if the WHO (1995) risk coefficient is used with a threshold of 60 ppb then the number of additional admissions is very similar (at 172) to the best estimate using the relative risk coefficient of Ponce de Leon *et al* (1996) at a threshold of 50 ppb.

Additional time series studies (Anderson pers. comm.) have recently been completed examining the relationship between daily emergency admissions for lower respiratory disease and the daily maximum of 8-hour running mean ozone concentrations. Analysis have been carried out for London and five additional areas of southern Britain, with each centred on the site of a monitoring station. A meta-analysis has been performed and a single combined coefficient, very close to that found by Ponce de Leon *et al* (1996) has been obtained. The relative risk coefficient of Ponce de Leon *et al* was derived from fixed 8-hour mean (0900 - 1600) ozone concentrations at a monitoring site in Central London. The similar coefficients obtained in these two studies supports the use of a.coefficient derived for London in both urban and rural locations in the UK.

Uncertainties due to mapping procedure

Figure 7.23 shows the daily and cumulative number of additional admissions due to ozone for the summer of 1993. The bulk of the additional admissions were estimated to have taken place on just a small number of ozone episode days. The influence of the mapping procedure on the estimated number of admissions has therefore been investigated by calculating admissions

for a range of mapping methods for just six days. These six days are listed in Table 7.4 and contributed almost 60% of the best estimate of the number of additional admissions of 184. The admissions calculation was repeated for these six days with three different mapping procedures in addition to the 'maps as used' in the calculation of the best estimate. These mapping methods differed in the way that ozone concentration in urban areas were calculated.

(a) **maps as used.** Ozone concentrations in urban areas were calculated from a map of the strength of urban influence factor, a, which was derived from urban ozone measurements where these were available.

(b) **a = 0.** Ozone concentrations in urban areas were assumed to be the same as in the surrounding rural areas: no urban effect.

(c) **a = 0.5.** A constant a value of 0.5 was assumed over the whole of the country: the urban ozone concentration was therefore given by

urban O_3 = (rural interpolated O_3) x (0.5 - 0.5 *(urblc))

giving an ozone concentration of a half the rural value for an entirely urban grid square.

(d) **a = 1.0.** A constant a value of 1.0 was assumed over the whole of the country: the urban ozone concentration was therefore given by

urban ozone = (rural interpolated ozone) x (urblc)

giving an ozone concentration of zero for an entirely urban grid square: the maximum urban effect.

It is instructive to look at each day in turn

- 23/05/93. This was a Sunday with ozone concentration between 50 and 60 ppb across most of the country. a values in the 'maps as used' were low in southern England and higher (a stronger urban influence, leading to lower ozone concentrations) elsewhere. Overall the 'maps as used' estimate of admissions was slightly higher than for maps with a constant a value of 0.5.
- 24/05/93. The maps with different treatments of urban areas for this weekday are shown in Figure 7.24. Ozone concentrations were slightly higher in rural areas than on 23/05/93 but urban concentrations were lower because it was a weekday. Increasing the a factor from 0.5 to 1.0 has only a small effect on the estimated number of hospital admissions for GB. Reducing the urban ozone concentrations from values below 50 ppb to near zero has no effect on the estimated number of hospital admissions.
- 06/06/93. Another Sunday, this time ozone concentrations were elevated across southern and central England only. Measured ozone concentrations in urban areas were similar to those in rural areas, leading to a 'map as used' estimate of admissions close to the estimate for the map with a = 0: with no urban effect.
- 08/06/93. Elevated ozone concentrations were again confined to southern and central England. Ozone concentrations were higher in rural areas than on 06/06/93 but urban concentrations were lower.
- 09/06/93. Ozone concentrations were elevated across all rural areas in GB. Ozone concentrations in urban areas were considerably lower than in surrounding rural areas but concentrations were so high that even a map with maximum urban influence gave an estimate of 29 hospital admissions.
- 10/06/93. Ozone concentrations were lower than on 09/06/93. Urban influence factors were close to 1.0 in London and the Midlands.

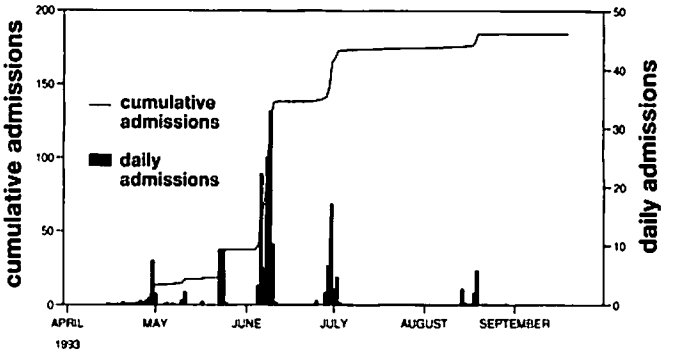


Figure 7.23 Additional hospital admissions due to ozone during 1993.

The choice of calculation method for ozone concentrations in urban areas does make a difference to the estimated number of additional hospital admissions. The estimated number of admissions varied from 172% (no urban effect) to 56% (maximum urban effect) of the 'maps as used' number of admissions for the six days studied in detail.

Uncertainties due to altitude variations in ozone concentrations

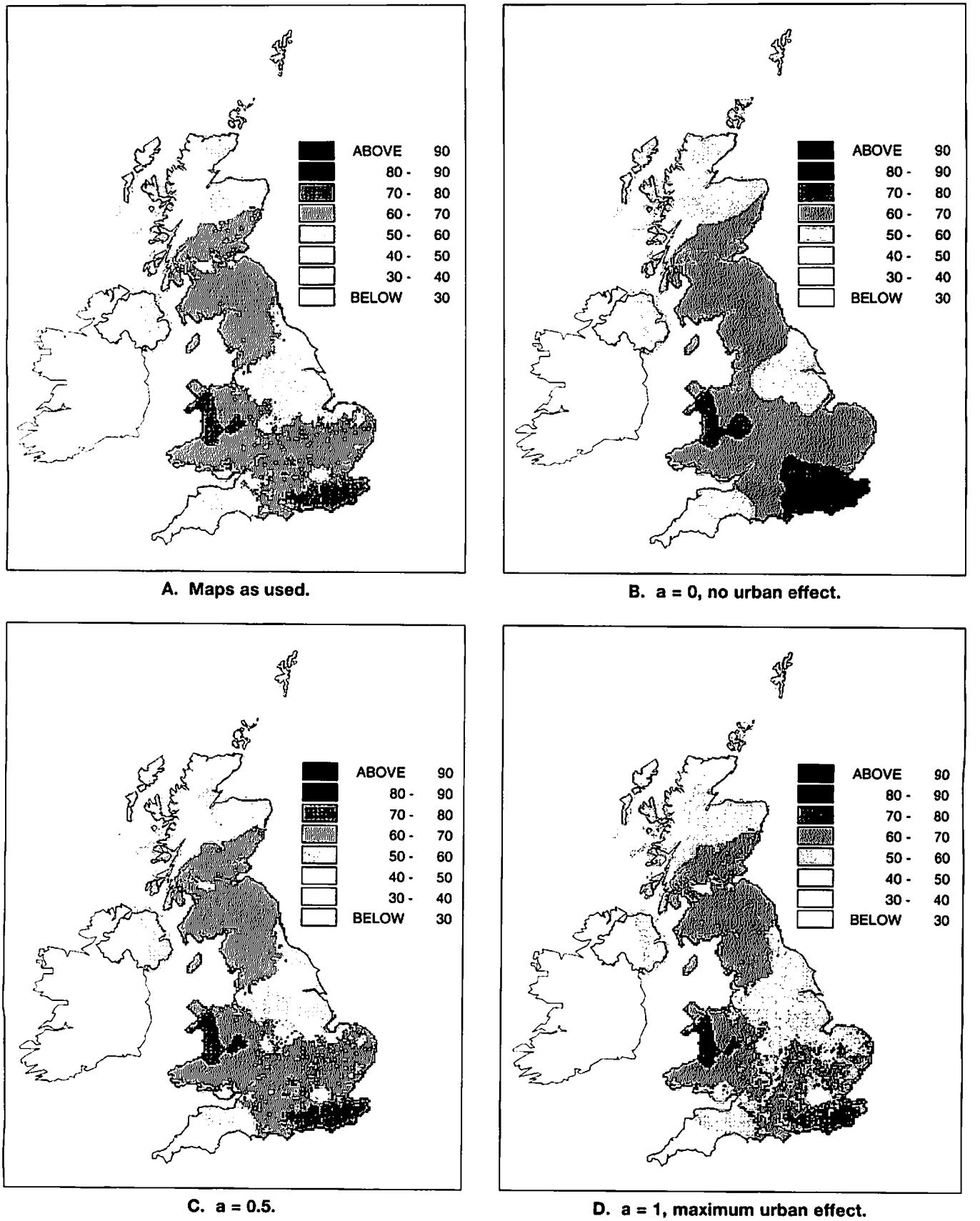
Ozone concentrations tend to be greater at higher altitudes than at lower altitudes, particularly at night which leads to a strong dependence of statistics such as annual mean ozone and the number of hours above a particular ozone concentration on altitude. The daily maximum of 8-hour running mean ozone concentration will generally occur during the day so the influence of altitude on this statistic will tend to be small. For example for the two monitoring sites of Great Dun Fell and Wharleycroft, which differ in altitude by over 600 m, the means of the daily maximum of running 8-hour average ozone for the summer of 1993 were 38.37 ppb and 37.34 ppb respectively. For days with a measured daily maximum of running 8-hour average ozone of ≥ 50 ppb at Great Dun Fell (the site at higher altitude) means of the daily maximum of running 8-hour average ozone were 66.94 ppb at Great Dun Fell and 61.00 ppb at Wharleycroft. For days with a measured daily maximum of running 8-hour average ozone of (≥50 ppb at Wharleycroft (the site at lower altitude) means of the daily maximum of running 8-hour average ozone were very similar (61.26 ppb at Great Dun Fell and 61.55 ppb at Wharleycroft).

The effects of altitude on ozone concentrations have not been taken into account in the mapping procedures in this current study. The influence of altitude could be

incorporated into the mapping procedure by comparing the daily maximum of running 8-hour mean ozone concentrations calculated for 'well mixed' day time periods with those calculated for complete 24 hour periods (see Chapter 3, Section 3.4.3).

7.3.4.8 Interpretation of Health Impact Findings

An increase in hospital admissions for respiratory diseases associated with increases in ozone concentration should be regarded as an indicator of health effect rather than as the whole extent of any effect.



A. Maps as used.

B. a = 0, no urban effect.

C. a = 0.5.

D. a = 1, maximum urban effect.

Figure 7.24 Maps of maximum 8-hour running mean ozone, ppb, across the UK for the 24th of May, 1993.

For every hospital admission for lower respiratory disease there are about 60 cases who consult their GP but are not admitted. Many more episodes of asthma and other lower respiratory problems such as bronchitis do not lead to a consultation at all. Admissions therefore represent the tip of a pyramid of severity. The increase in admissions associated with ozone could represent a small shift in the severity of all episodes of lower respiratory disease or, more likely, in the severity of a smaller group of cases who happen for reasons as yet unknown to react more strongly to ozone.

Another important question about the nature of the health impact concerns whether these extra admissions are inevitable even without ozone exposure, or whether they are additional to the usual rate of admission. In the former case, it is postulated that ozone accelerates the progression of the clinical condition so that admission is brought forward. In the latter case, it is postulated that patients are admitted to hospital who would not have been admitted in the absence of ozone exposure. Only in the latter case is there an additional burden on the health service. It is not possible to determine which of these two alternatives is the most likely using the available methods of analysis of epidemiology data.

The clustering of highest ozone days into a small number of episodes, each of several days duration (see Figure 7.23), might lead to a 'saturation' of the health impact. If all (or most) of the susceptible subjects in a region responded at the beginning of a few-days episode then the expectation of additional hospital admissions towards the end of an episode may not be correct.

The calculated number of additional hospital admissions is extremely sensitive to the value of the threshold ozone concentration used and this is the cause of one of the largest uncertainties in the estimates. The analysis was, therefore repeated using an alternative approach in which we did not assume a threshold and estimated excess admissions across the whole range of ozone exposures. This led to estimates of effect which were of an order of magnitude greater than those obtained using the threshold approach. Individuals probably vary in their threshold level and are exposed to a wider range of pollutant concentrations than indicated by monitoring data. This argues against the threshold approach at the population level and was the rationale for the WHO decision to describe exposure response relationships to ozone and other pollutants as a continuum (WHO, 1995). We believe that the most appropriate estimate is in the range between the threshold and no threshold estimates.

For these reasons, it is unwise to conclude that the small increase in admissions indicated by this current analysis represents the only effect on morbidity which may be associated with ozone. Conversely, it is also unwise to assume that all of the additional admissions constitute an increase in health service costs.

7.3.5 Revision of WHO Air Quality Guidelines for Ozone

In 1987, WHO recommended the following guidelines for ozone (WHO, 1987)

1 hour averaging period: 76-100 ppb
8 hour averaging period: 50-60 ppb.

In 1994 a WHO Expert Group was convened to review the guidelines recommended for the major (classical) air pollutants (WHO, 1995). This Group considered recent developments in ozone toxicology and recommended revision of the Guidelines. In particular the Group were impressed by the importance of duration of exposure in predicting the effects of exposure to a given concentration of ozone. This has been touched on above. As a result of this and the perception that concentrations of ozone were likely to be raised for a number of hours on warm summer days, the 1 hour guideline was abandoned. The 8 hour guideline was revised to 60 ppb in line with the enlarged data base on effects now available. It was accepted at a later meeting of WHO experts (1996) that effects of less significance might occur at concentrations of less than 60 ppb (as an 8 hour mean).

In addition to the Guideline an exposure response curve was defined in tabular form for the effects of both 1 and 8 hour exposure to ozone. These data are displayed in Tables 7.5 and 7.6.

The Group provided the following comments on Table 7.5:

> "The values presented in Table 7.5 assume a linear relationship between ozone concentration and health outcome. However, uncertainties exist concerning the forms of these relationships, and it is unclear whether similar response slopes can be expected at widely different ambient ozone levels. In the event that such relationships are curvilinear (ie concave upward) the benefits of lowering ozone concentrations are likely to be greatest when the average ambient level is higher. Consequently if ambient ozone concentrations are already low, the benefits of lowering concentrations may be less than would be suggested by Table 7.6."

In 1994 the Department of the Environment's Expert Panel on Air Quality Standards (EPAQS) published a recommendation for an Air Quality Standard for ozone (EPAQS, 1994). The recommended standard was expressed as an eight hour moving average concentration of 50 ppb. The Panel recognised that the response to ozone depended on both the concentration to which people are exposed and to the length of exposure. It was argued that on warm summer days exposure outdoor for 8 hours was not unlikely. It was felt that defining a particular averaging period would be an error as it was not easy to predict the precise 8 hour period during which the average concentration of ozone would peak on any given day; a moving average was thus recommended. This makes exceedance of the recommended standard more likely. In deciding on a concentration of 50 ppb for the recommended standard the Panel argued that though the lowest concentration of ozone which had been shown to produce effects on lung function as a result of an experimental exposure of about 6 hours was 80 ppb, a margin of safety should be included in recommending a standard. The relationship between likely exceedances of the

recommended standard and the peak 8 hour concentration of ozone likely to occur was also explored. It was noted that if the recommended standard is exceeded on less than 10 days per year, at any one site, one would not expect, in most years, the highest 8-hour concentration to exceed 100 ppb. A figure showing this relationship was included in the report and is reproduced here as Figure 7.25, with the period of data used extended to 1995.

It will be seen that the EPAQS recommendation differs from the Guideline recommended by the WHO Expert Group involved in updating the WHO Air Quality Guidelines for Europe. This is not unexpected as different groups of experts are likely to ascribe different weightings to different facets of the available evidence and to differ regarding acceptable safety margins. For example, workers familiar with experimental studies might not be impressed by an average decrement in FEV_1 of perhaps 5-10%. Epidemiologists, on the other hand, with their wider appreciation of the range of sensitivity likely to occur in a population and of the possibility of such an average response shifting a substantial group of people into an "at risk" category, might weight such a response more heavily. The attention paid by EPAQS to limiting the number of times the 8 hour average concentration is likely to exceed 100 ppb represented a novel approach which had not been considered by the WHO Expert Group.

Table 7.5 Health outcomes associated with controlled ozone exposures.

Health outcome	Ozone concentration ($\mu g/m^3$) at which the health outcome is expected.	
	1 hour average	8 hour average
Pulmonary function change (decrease in forced expiratory volume in 1 sec in active, healthy, outdoors, most sensitive 10% of population)		
5%	250	120
10%	350	160
20%	500	240
Inflammatory changes (neutrophil influx in lungs of healthy, young adults exercising at >40 l/min outdoors)		
twofold increase	400	180
fourfold increase	600	250
eightfold increase	800	320

Table 7.6 Health outcomes associated with changes in peak daily ambient ozone concentrations in epidemiological studies.

Health outcome	Change in 1 h $O_3(\mu g/m^3)$	Change in 8 h $O_3(\mu g/m^3)$
Symptom exacerbations among healthy children and adults or astmatics - normal activitiy		
25% increase	200	100
50% increase	400	200
100% increase	800	300
Hospital admissions for respiratory conditions [a]		
5% increase	30	25
10% increase	60	50
20% increase	120	100

a Given the high correlation of 1-hour and 8-hour ozone concentrations in field studies, an improvement in health risk associated with decreasing 1- or 8- hour ozone levels should be almost identical.

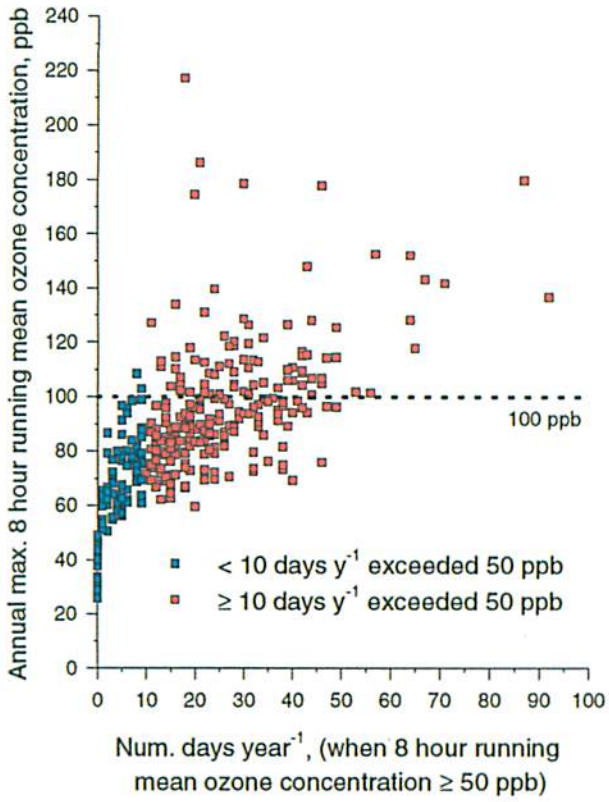


Figure 7.25 A plot of the number of days in any one year on which the 8 hour running mean exceeded 50 ppb versus the maximum 8 hour running mean in that year, for every site in the PORG database from 1972 to 1995.

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8. OZONE IN A EUROPEAN PERSPECTIVE

- Ozone is a major gaseous pollutant throughout Europe and ambient concentrations regularly exceed thresholds for effects on vegetation and human health during the summer in most countries.
- The magnitude of exceedances of effect thresholds for both crops and human health increases along a gradient from the UK towards central Europe. In this respect the UK, along with the Scandinavian countries, are the areas least affected by episodes of elevated ozone in Europe.
- To date there are no high resolution ozone concentration or exceedance maps for the whole of Europe, although such maps have been produced by a few countries.
- The transport distances of pollutants and their precursors and the timescales for chemical production of ozone lead to long range transport of photochemical oxidants throughout Europe. As a consequence we share the same air and its associated pollutants. Policies to reduce the frequency and magnitude of elevated ozone episodes require control measures throughout Europe.
- Policies to reduce the Northern hemisphere tropospheric background ozone concentration would require control measures throughout the Northern hemisphere.
- The European ozone monitoring data (1980 - 94) show no consistent trends in mean concentrations throughout the period. A small reduction in mean concentration has been reported for the Netherlands, although the underlying cause is unclear.

8.1 Introduction

In this chapter a very brief description of the climatology of surface ozone throughout Europe is presented to provide the broader geographical context for UK ozone data presented in Chapter 3. Direct, high quality measurements of ozone have only been routinely made during the last 3 decades, the longer term trends for the century have been subject to considerable debate. However it is generally accepted that tropospheric ozone concentrations have increased substantially over Europe during the 20th century with an increase in ground level mean annual ozone concentrations from 10-15 ppb at the turn of the century to *ca* 30 ppb today (Voltz & Kley, 1988; Anfossi *et al*, 1991). The increase in ozone concentrations does not only occur at ground level but is observable throughout the troposphere. (Figure 8.1; Staehelin *et al* 1994).

Model calculations show that the increase in ozone concentrations is consistent with anthropogenic emissions of the precursors; nitrogen oxides (NO_x), volatile organic compounds (VOC), carbon monoxide (CO) and methane (CH_4) (Isaksen and Hov 1987).

8.2 The Ozone Climatology of Europe

Although more than 1000 ozone monitoring stations operate in the 15 member states of the European Union, there has been no comprehensive analysis of the ozone climatology of Europe. Analyses are described by Simpson, 1991, Dollard *et al* 1995 and EEA, 1996 but these assessments provide a partial coverage of the area and have limited spatial resolution. In some countries the analysis of monitoring data has provided a satisfactory basis for maps of mean concentration and exceedances of thresholds for health and vegetation effects. This report describes a procedure used to generate detailed maps of ozone exposure of natural vegetation, forests and crops, throughout the UK. Similar analysis have been provided for Switzerland (Fuhrer, 1996) and Scandinavia (Lövblad *et al*, 1996).

European photochemical oxidant data has been collated and analysed by EMEP (1996), EUROTRAC (Borrell *et al*, 1997) and the EEA (1996). EMEP and EUROTRAC have produced substantial reviews of recent measurements and research initiatives. It is not the purpose of this brief chapter to review these documents, or the data. However, the complexity of the underlying science

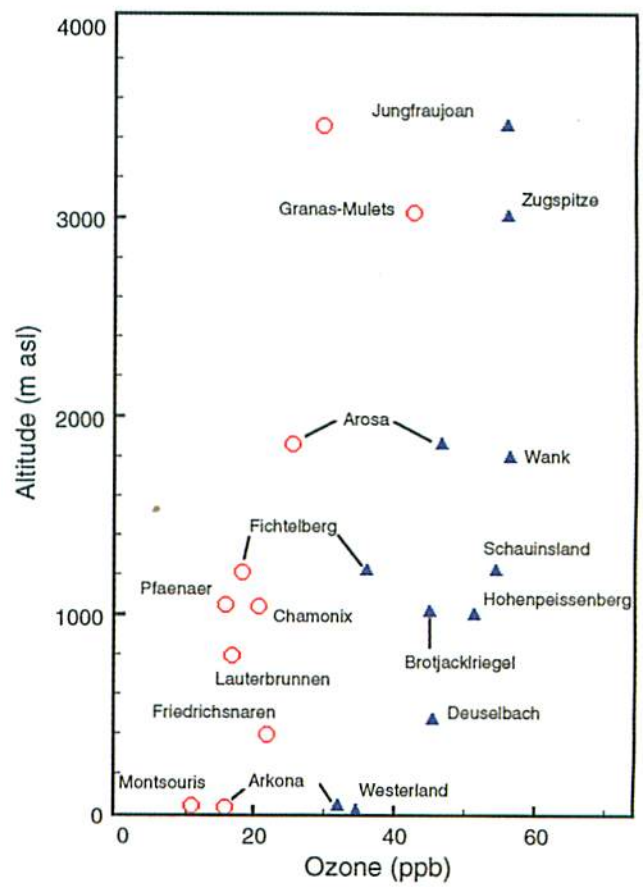

Figure 8.1 Surface ozone concentrations observed in late summer at different locations in Europe. The red open circles summarise historic data collected before and during the 1950s, the blue triangles are from measurements made after 1988. The data have been plotted against site altitude.

Table 8.1 Internal ozone production in Europe April-September 1989 calculated as the difference in daytime ozone concentration (0900-2100) between the actual monitoring station and the mean of the concentrations at four remote sites in Europe.

Monitoring area	Number of stations	Internal ozone production (ppb)
Continental Europe - remote sites	6	5 – 30
Continental Europe - "urban sites"	8	-5 – +10
British Isles - S 54° N	9	-13 – +8
British Isles - N 54° N	6	0 – 3
Scandinavia - S 62° N	12	5 – 8
Scandinavia - N 62° N	6	-3 – +3

and importance to policy development at the European scale should increase the analysis and interpretation of the available data and develop closer links between the monitoring and air chemistry community and the effects assessment communities. In particular, analysis of the extensive ozone data for Europe to produce appropriate maps of ozone exposure and dose is a clear priority for the assessment of effects.

Ozone data are mainly available from central and Northwest Europe, where ozone is monitored at more than 100 rural sites, within the EMEP and TOR networks. The monitoring data show a clear gradient in rural summertime concentrations (both mean daytime values and the frequency in exceedance of the thresholds 40 ppb, 80 ppb and 100 ppb from the NW (and N) towards central Europe. Thus, the British Isles and Scandinavia show generally lower summer daytime ozone concentrations than the south of France, Germany, Switzerland, and other countries of central and southern Europe.

The elevated concentrations in central Europe are due to photochemical episodes, during which ozone concentrations may reach 200-300 µg m^{-3} (~100-150 ppb). The ozone episodes occur during high pressure conditions over continental Europe and within these regions of high pressure, concentrations of precursors and oxidants are accumulated over periods of typically 2 to 10 days. The ozone production increases the continental summertime mean by 10-30 ppb relative to concentrations at the fringe of Europe. (Table 8.1; Beck and Grennfelt 1993, 1994, Borrell *et al* 1996).

The mean annual maxima for individual stations for the period 1988 to 1994 show that the peak values occur in countries with latitudes less than 50° N including Italy, Slovenia, Austria and Switzerland. (Figure 8.2). While considerable inter station variability is present there is a clear trend towards smaller mean maxima as latitude increases from 50° N to 80° N The intermediate values for sites in the Iberian peninsula reflect the less polluted nature of the air from the Atlantic or much of this region. However, in Spain and Portugal some sites show very large exceedances of critical level thresholds.

Monitoring stations at the outskirts of Europe often show a clear spring peak between 50° N and *ca* 70° N, starting in February and reaching its maximum in April/May (Grennfelt and Schjoldager 1984, Solberg *et al* 1996). Even stations in central Europe show a spring maximum which becomes more evident if data from European photochemical ozone episodes are filtered out, i.e. the spring peak appears to be of a different origin than the summertime peaks. North of 70° N the spring peak is less obvious and it is likely that ozone decomposition processes in the spring and early summer change the pattern.

The precise cause of the spring maximum is not well understood. There are indications that the maximum may be partially caused by tropospheric production from precursors accumulated over the polar region during the winter. Lindskog (1996) shows that there is a very close relationship between the ozone build-up in the early spring and the disappearance of the accumulated

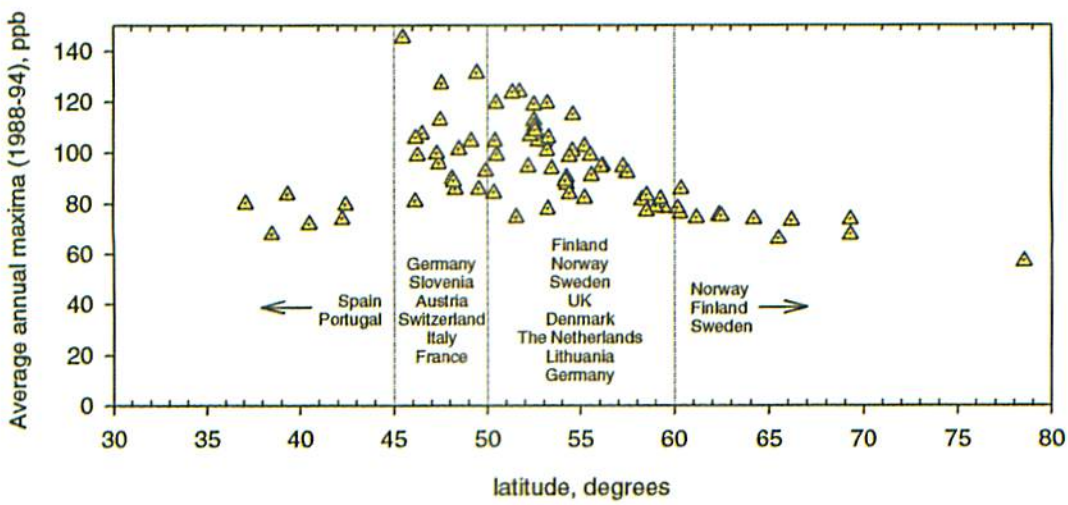

Figure 8.2 Average of 1988 to 1994 annual maxima at EMEP ozone monitoring sites, plotted against the sites latitude (only years with at least 75% data capture are included).

VOCs. The data indicate that for a loss of 1 ppb C, there is an increase in ozone of *ca* 1 ppb.

The simple pattern of a gradual increase in the frequency of episodes of photochemical oxidant production from the NW and N of Europe towards the central areas provides a convenient description of the average properties of the monitoring data. Such simple patterns do not extend into the Mediterranean regions. Mediterranean regions and the Iberian peninsula experience long periods of settled spring and summer weather in which sea breeze and strong convection over the land interact with the topography to produce very different geographical patterns in ozone exposure (Millán, 1994). Such large differences in the climatology of these regions preclude extrapolation of the spatial patterns of ozone from Northern Europe into these areas.

8.3 Trends in Tropospheric Ozone Concentration in Europe

In Europe, ozone has been monitored routinely for 10 years at a fairly large number of sites. Trend analysis show no uniform picture for the whole of Europe. However, there are important regional trends. In the Netherlands, there are strong indications of a recent downward trend. Roemer (1996) has shown a downward trend in yearly mean concentrations of 0.4 - 1.6% per year for nine sites in the Netherlands between 1981 and 1994. The trend is observable in both summer and winter means as well as in maximum values. For other parts of Europe the results are more scattered. Roemer has also calculated the trends in ozone concentrations at sites in Germany and Scandinavia. For Northern Germany, Roemer also concludes that a downward trend is detectable for the period 1980-94 based on data from rural sites. In an updating of the German data in connection with this report we found a slight positive trend if data from the period 1984-95 were considered. Data from the monitoring stations in Scandinavia and Switzerland (BUWAL 1994) show no trend or in some cases and upward trend. At the only East European station reporting long term data in ozone (Preilla in Lithuania) a clear upward trend of 2.6% per year between 1982 and 1993 is observed. The conclusions that can be drawn from the long term data series is that more thorough evaluations are necessary to show and understand long term changes in ozone concentrations over Europe. Such evaluations are extremely important when assessing the outcome of the VOC protocol and other measures to reduce emissions.

Since 1980 a number of control measures have been undertaken in West Europe to reduce emissions of VOCs and nitrogen oxides. The magnitudes and outcomes of these measures vary between countries but in some countries it is reasonable to assume that emissions have decreased substantially (Berge *et al*, 1994). The control of anthropogenic emissions of VOC has probably been larger than that for NO_x leading to a decrease in the VOC/NO_x ratio. Large uncertainties in emission data, make it difficult to quantify the magnitude in these changes.

The question then is why the stations in the Netherlands show a clear downward trend in ozone while no clear trend is observed at any analysed continental station outside the Netherlands? The difference may be that all Dutch stations are lowland stations and are very influenced by local and mesoscale titration from nitric oxide.

Analysis and interpretation of trends in ozone at rural monitoring sites is complicated by the many factors that may potentially influence long term ozone concentrations. To assist in the analysis of these factors, detailed scrutiny has been given to the monitoring data from Mace Head, on the west coast of Ireland, for the period 1987-1996, inclusive.

Isentropic back trajectory analyses, EMEP daily sector allocations and simultaneous halocarbon measurements provide three independent and unambiguous methods of allocating air mass origins to each hourly mean measurement. Attention here is directed to those air masses which can be described as either "northern hemisphere background" or "European".

During the period 1990-1994, 61% of the hourly ozone measurements made at Mace Head were allocated to the background sector. The mean ozone concentration reported for these measurements was 34.9 ± 4.3 ppb and a significant downwards trend of -0.046 ±0.03 ppb per month or -1.6% per year was apparent over this period. However, looking over the entire 1987 - 1996 period it appears that background ozone concentrations, having declined over the 1990-1994 period, recovered during the 1995-1996 period. Over the 1990-1996 period, there has been an upwards trend of +0.092 ppb per year or +0.2% per year.

These changes in background ozone should be seen in the light of the global measurements of ozone and of the other major tropospheric trace gases. During the 1990-1994 period, the upwards trends in carbon dioxide, methane and nitrous oxide noted during the 1980's all slowed dramatically. These dramatic changes in trends have not been quantitatively accounted for, although they have been tentatively explained as a Mount Pinatubo effect (erupted in 1991). Here we see evidence of a corresponding impact on ozone. Subsequently, during 1994 and 1995, the upwards trends in all these tropospheric trace gases found during the 1980's have resumed, ozone included.

The trends in the ozone concentrations reported for "European" air masses during 1990-1994, at Mace Head, were significantly larger than for "background" air masses. The downwards trend in ozone approaches -0.12 ppb/month or -4.6% per year. Downward trends in carbon monoxide concentrations in "European" air masses have also continued with the trend over the 1990-1994 period reported as -1.2 ppb/month or -9% per year. During the 1987 - 1996 period the overall trend is downwards but with a much reduced trend of -0.0031 ppb per month or -1.3% per year.

The marked downwards trend in the mean ozone concentrations observed for European air masses during 1992-1994 has almost completely been made up during 1995 and 1996. The behaviour of ozone here appears to be following the broad scale meteorological patterns, with relatively poor summers giving reduced

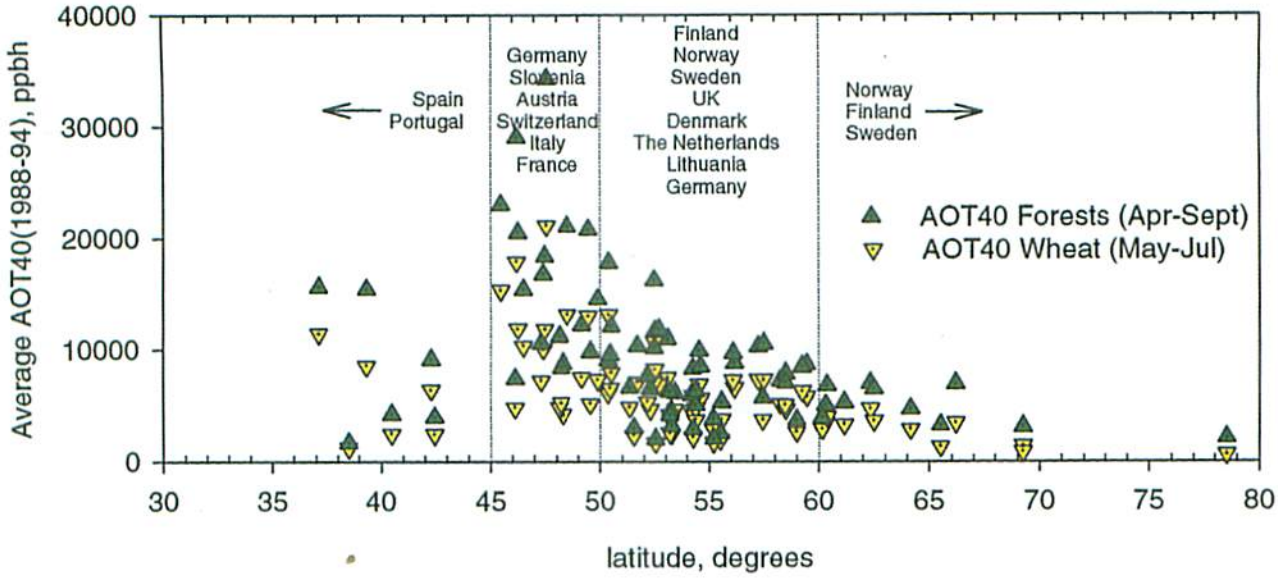

Figure 8.3 Average of 1988 to 1994 AOT40 values for daylight hours during April to September (forests) and May to July (wheat) at EMEP ozone monitoring sites, plotted against the sites latitude (only years with at least 75% data capture are included).

photochemical activity and so low summertime ozone levels at Mace Head and the warmer summers in 1995 and 1996 giving somewhat higher mean ozone concentrations.

Concentrations of methane and nitrous oxide in European air masses follow a similar pattern to ozone, supporting the conclusion that currently meteorology is having the largest influence on trends in Europe. Although reductions in precursor emissions from some European countries will have reduced the potential for ozone formation.

8.4 Critical Levels Exceedances

8.4.1 Exceedance of the Critical Levels for Vegetation

The critical levels for effects on vegetation were recently revised at a workshop in Kuopio. (Karenlampi & Skarby, 1996). For the critical levels for crops, the workshop essentially confirmed the conclusions from the previous workshop in Bern in 1993. Based on additional results it was recommended to use a critical level of 3000 ppb h AOT40 for a daytime 3 month mean May-July. Data should be averaged over 5 years to obtain satisfactory regional maps. For forests a critical level of 10,000 ppb h was set as daytime values for 6 months.

Maps of ozone concentration exceedances of the critical load for forests and crops have not been calculated using the same procedures for the whole of Europe as have been presented in this report for the UK due to a lack of appropriate data. The five year data set required to reduce inter-year variability for the mapping is only available for the well monitored counties. It is, however, important to identify the relative extent of exceedances of critical levels for vegetation and human health for the UK and other areas of Europe.

Figure 8.3 provides a summary of the average AOT40 values for 1988 to 1994 at individual sites and shows that the majority of sites exceed the arable cropland critical levels, but that inter-site variability in the AOT40 values is very large. Also clear in the data is a trend of increasing exceedances with decreasing latitude and the largest exceedances in Germany, Switzerland, Slovenia, Austria and Italy. These data are entirely consistent with the regional trend in the UK with AOT40 increasing along a NW to SE transect through the country.

In a North-South transect of ozone monitoring stations from Arctic Scandinavia to the Mediterranean, Grennfelt and Beck (1994) show a pronounced gradient of increasing AOT40 levels (Table 8.2). The increase in exposure to concentrations in excess of 40 ppb is typically an order of magnitude, from 30 to 1000 ppb h $month^{-1}$ in N Scandinavia to 1500 to 10,000 ppb h $month^{-1}$ in S Europe.

The limited measured ozone data may be mapped using simple linear interpolation techniques which do not incorporate altitude effects. These have been applied to the available rural monitoring stations for the period 1990 to 1994 inclusive to map data for AOT40 forest and arable crops. The forest AOT40 map (Figure 8.4) shows exceedance of the 10,000 ppb h threshold over the majority of the mapped area of continental Europe with a gradual increase along a north south transect and large exceedances in southern Germany, France, Switzerland and Italy. The arable crop exceedance map (Figure 8.5) shows an equally simple pattern with exceedances of the threshold (3000 ppb h) from central England southwards into Europe and very large exceedances in Italy. These simple maps show that the north-south patterns in exceedance of critical loads in the UK (Chapter 7) are consistent with those observed in continental Europe and that the scale of effects in the UK are likely to be at the lower end of the range of effects in Europe.

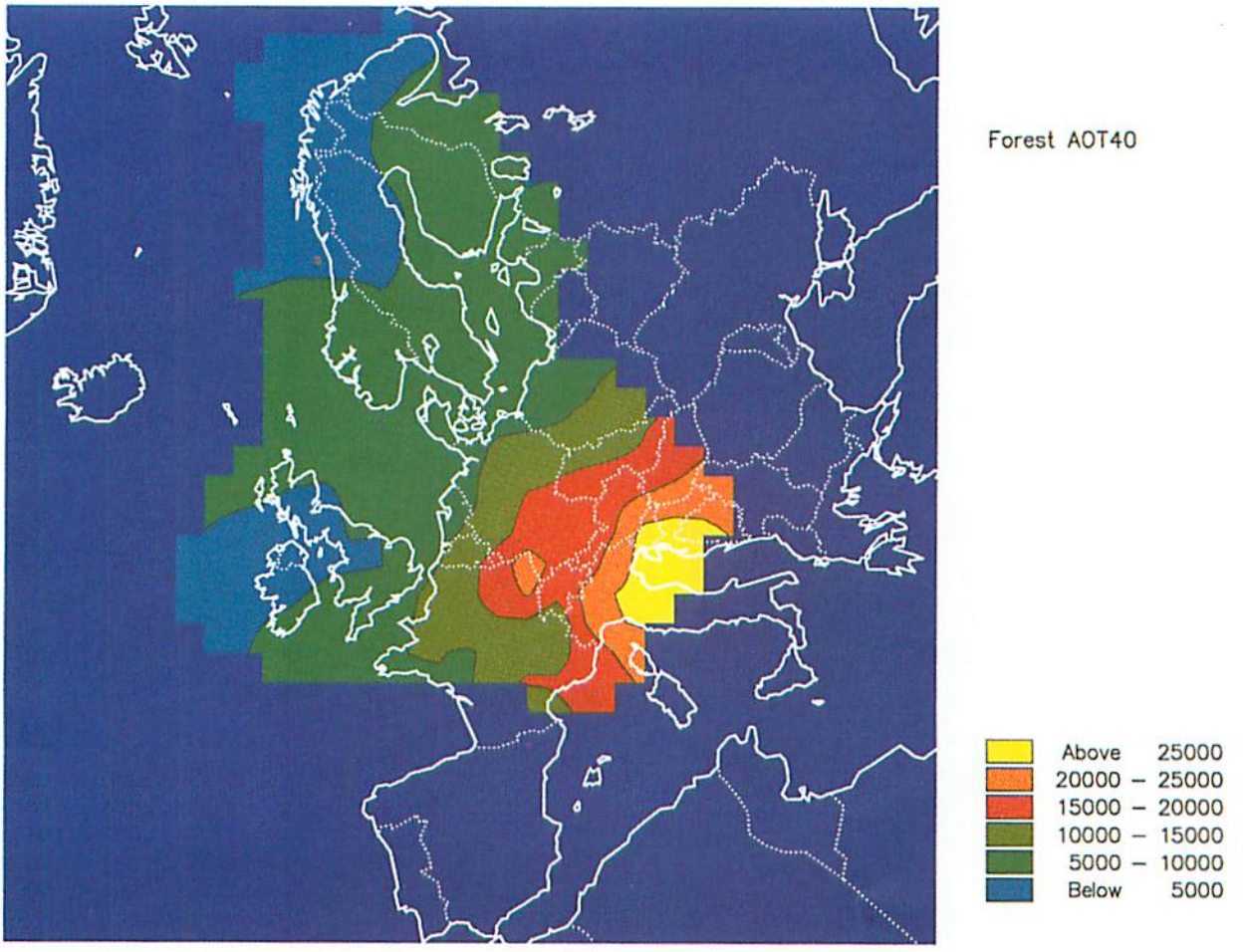

Figure 8.4 AOT40 for forests (April-September daylight hours), mapped from 1990-94 averaged measurements.

8.4.2 Exceedances of Health Effects Thresholds in Europe

A human health protective threshold for effects of ozone defined by EPAQS (1994) has been developed. This is based on an 8 hour running mean of 50 ppb and can be used to examine the spatial variability in exceedance for the EMEP monitoring statistics throughout Europe.

The degree of exceedance can be assessed by counting the total number of 8 hour running mean periods or days on which the critical level is exceeded. The data in Figure 8.6 show that largest exceedances are in areas south of latitude 50° N, although a substantial exposure to concentrations in excess of 50 ppb are also present between 50° N and 60° N.

8.4.3 Observed and EMEP Model Calculated AOT40 Values for Ozone

Because of a general lack of high quality ozone measurements across Europe and because much of the interest in ozone from the policy perspective is its response to emission controls, the analysis of policy options will be done within the UN ECE with EMEP model ozone data. Since the only approach developed to date appears to be to use AOT40 ozone values rather episodic peak ozone values, it is of interest to compare the EMEP model results for the April-September 1990 period with the EMEP ozone network results. This is done in two stages, across Europe and for the United Kingdom.

Table 8.3 presents the model and observations in some detail for the United Kingdom, showing a significant

Table 8.2 Exceedances (ppb h) above 40 ppb at TOR and EMEP sites below 1000 m above sea level, 3 month periods during daylight hours April - September 1989. N denotes number of stations. (Grennfelt and Beck, 1994).

Area	N	Number of ppb.h exceeding 40 ppb			
		Apr.-Jun.	May-Jul.	Jun.-Aug.	Jul.-Sep.
N Scandinavia > 62° N	6	900-4600	100-3700	200-2200	0-700
S Scandinavia > 62° N UK > 54° N	20	2200-8200	2700-8600	800-6400	400-3500
UK < 54° N	9	1600-11800	2300-13000	1500-9700	400-6300
European Continent, Coastal	4	4900-197005	400-19900	3500-14200	3000-8100
European Continent, Inland	18	2700-23800	4200-28700	3600-24200	3400-17800

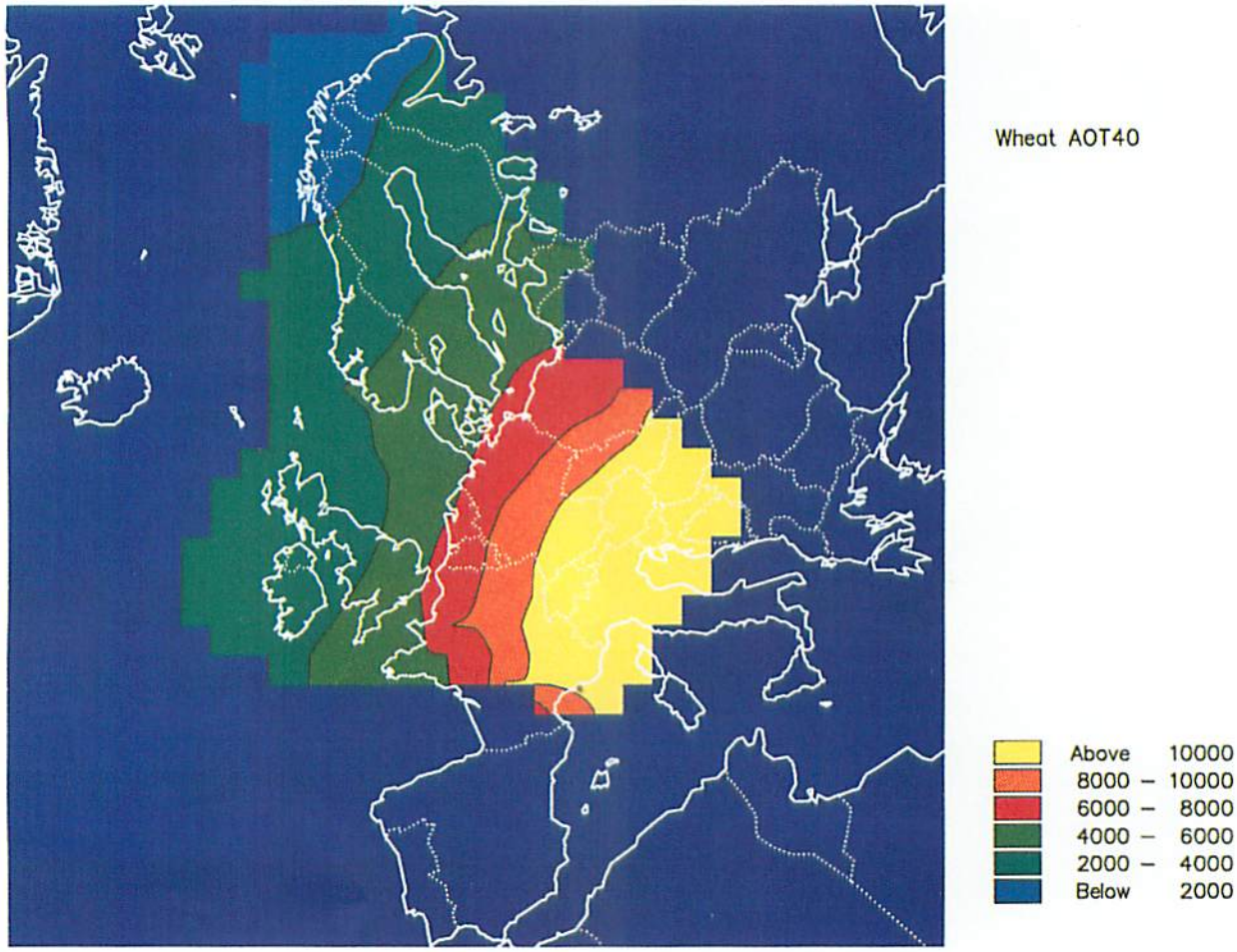

Figure 8.5 AOT40 for wheat (May-July daylight hours), mapped from 1990-94 averaged measurements.

overestimation. It is not clear whether the overestimation of this statistic is more due to overestimation of the tropospheric ozone baseline, or to duration of the daily peak value or due to the overestimation of regional scale photochemical ozone production, generally across Europe or on the trajectories to UK arrival points.

8.5 Precursors

8.5.1 NO_x

Nitrogen oxides concentrations (primarily NO_2) are measured at a number of stations in Europe. The EMEP network has as one of its objectives the quantification of regional concentration patterns of major gaseous

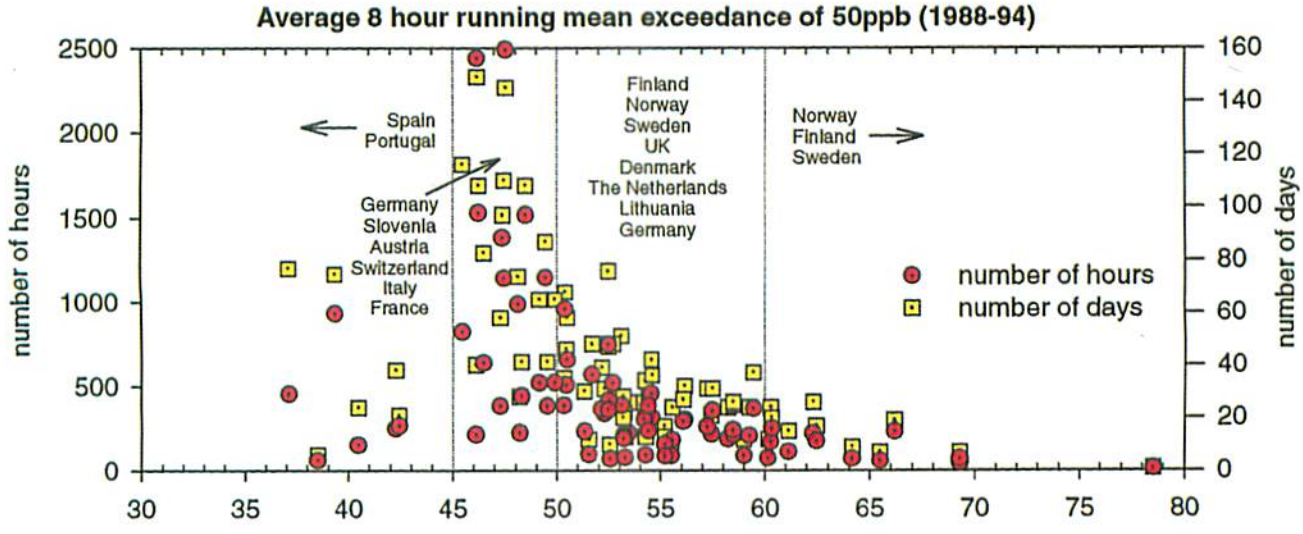

Figure 8.6 Average of the number of hours and days per year on which the eight hour running mean exceeds 50 ppb, for 1988 to 1994 at EMEP ozone monitoring sites, plotted against site latitude (only years with at least 75% data capture are included).

Table 8.3 Apr-Sept 1990 AOT40 from the EMEP model and EMEP database.

Site	ppb hours	
	Modelled	Observed
Eskdalemuir	19656	6973
Lough Navar	12768	4819
Yarner Wood	34482	22615
High Muffles	2515	9970
Strath Vaich	11118	6596
Aston Hill	23466	18837
Bottesford	30996	6331
Bush	18348	5231
Glazebury	17538	5085
Great Dun Fell	22722	13492
Harwell	31020	12558
Ladybower	14874	10244
Lullington Heath	39540	25168
Sibton	35628	11972
Stevenage	30828	8231
Wharleycroft	22632	7439

pollutants through Europe. For nitrogen dioxide which has been part of the monitoring programme for several years, the network is still too sparse and the accuracy of the measurements too low to provide a comprehensive picture of the concentrations for all Europe (Hjellbrekke *et al* 1993). Data from West and central Europe (with the exception of UK and Italy) show regional maxima in the Iberian Peninsula and over the Benelux countries. The yearly means at stations in these areas exceed 20 μgm^{-3}. NO_2 concentrations are generally higher in the winter compared to the summer. The ratios between the highest and the lowest monthly means are normally in the range of 2-4.

8.5.2 Volatile Organic Compounds

Monitoring of volatile organic compounds has recently been included in EMEP as a pilot programme, in which sampling is performed at a limited number of stations (e.g. Solberg *et al* 1995). VOC monitoring was also an important part in the recently finished EUROTRAC programme on Tropospheric Ozone Research (TOR) (e.g. Lindskog *et al* 1995). The concentration pattern over Europe shows for most situations higher concentrations in central Europe compared to the outskirts. The atmospheric behaviour is, however, somewhat different to nitrogen oxides, especially for the VOC with low reactivity, e.g. ethane and propane. For these compounds, there is an accumulation of VOCs over the polar regions during the winter months resulting in comparatively small differences between continental and northern stations, Solberg *et al* 1995. There are still too few years of data to allow statistical evaluations of trends in concentrations.

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9. PHOTOCHEMICAL OXIDANTS AND THE EFFECTS OF EMISSION CONTROLS

- Regional scale ozone formation and its control is an important policy issue in a number of international policy fora, including in particular, the UN ECE and the European Union.
- The work of the UN ECE has concentrated mainly on the impacts of ozone on crops and trees and has introduced the concept of AOT40 to characterise critical exposure levels of ozone. It is likely that reductions in NO_x and hydrocarbon emissions approaching the maximum feasible will be required if these critical levels are not to be exceeded in future years across Europe.
- The work of the European Union has focused mainly on human health effects and the role played by motor vehicles and their fuels in the deterioration of urban air quality. Proposals are being drawn up for emission and fuel quality standards for the year 2000 and beyond. The Commission has adopted an air quality objective of 90 ppb, 99-percentile hourly mean ozone concentration, a level which is not normally exceeded in the United Kingdom except in the most photochemically active summers.
- The National Air Quality Strategy has set a challenging health-based provisional air quality objective for the UK of 50 ppb as an 8-hour rolling mean expressed as a 97th percentile. VOC and NO_x emission reductions approaching the limits of technical and economic feasibility will be required, going far beyond the current policies, if the ozone quality objective in the National Air Quality Strategy is to be met in the future.
- Further consideration will need to be given to background tropospheric ozone if strict vegetation-based environmental criteria expressed in AOT40 terms are not to be exceeded in the UK and in the rest of Europe. This will require action on ozone precursor emissions at a global scale.

9.1 Introduction

The regional scale formation and long range transport of ozone has long been recognised as a significant problem for air quality policy in Europe. Initially, policy on ozone was coordinated through the Organisation for Economic Cooperation and Development (OECD) in Paris, but during the 1980's focus shifted to the United Nations Economic Commission for Europe (UN ECE) in Geneva. More recently, the Commission for the European Communities has entered the ozone policy scene by taking responsibility for vehicle exhaust emission limits and promulgating air quality directives. Assessment of the human health impacts of ozone and of urban air quality policies has been a matter for the World Health Organisation in Geneva and with its European Office in Copenhagen.

9.2 The Work of the UN ECE on Ozone

The UN ECE has provided a policy focus for air quality through its international convention on Long Range Transboundary Air Pollution (LRTAP). This convention has established activities on the exchange of information between its member states concerning air quality, its environmental impacts and its control. The UN ECE has established the European Monitoring and Evaluation (EMEP) research programme through which air and precipitation quality monitoring networks, long range transport models and emission inventories have been established (United Nations, 1985). In 1987, this co-ordinated research activity led to the formulation of the Sofia Protocol to the LRTAP convention. In this Protocol, signatories are committed to returning annual NO_x emissions to their 1987 levels by the year 1994, (United Nations ,1988). This NO_x Protocol is underpinned by a considerable body of understanding of the role of NO_x in regional ozone formation and its long range transport and of the adverse environmental impacts of elevated ozone levels on human health.

NO_x is not the sole ozone precursor and the UN ECE then turned its attention to VOCs. In 1991, continued policy formulation work on ozone led to the formulation of the Geneva Protocol to the LRTAP convention. In this Protocol, signatories are committed to a 30% reduction in their VOC emissions by 1999 on their 1990 levels, (United Nations, 1991). It was envisaged that this level of VOC emission reduction would be achieved by the introduction of three-way catalysts on motor vehicles. It has always been accepted by the UN ECE member states that the Sofia NO_x and Geneva VOC Protocols were the first steps in a coordinated policy response to the problem of the regional scale formation of ozone and its long range transport. Negotiations have begun on the second stage of the Sofia NO_x Protocol and the paragraphs which follow, identify the various elements of the assessment process involving ozone which will shape these negotiations.

The member states of the UN ECE have agreed that the negotiations for the second NO_x protocol will be based on the critical loads approach. In this approach, commitments to emission reductions must be based on the capacity to absorb the remaining pollution loads and the policies must be implemented in a scientifically rigorous and cost-effective manner. The critical levels for ozone have been established through a series of international scientific workshops dealing with the impacts of elevated ozone concentrations on forests and vegetation (Karenlampi and Skarby, 1996). These critical levels have been formulated using the AOT40 concept which defines the measure of ozone exposure through the accumulated time during which the hourly ozone concentration has exceeded a certain threshold concentration, taken to be 40 ppb. In this way ozone critical levels have been defined for forests and crops across Europe as a whole. These critical levels for ozone measure long term exposure to ozone over the period of up to six months and are sensitive to the

ozone levels both within recognised photochemical pollution episodes and without.

The UN ECE are preparing to use the EMEP photochemical oxidant model to relate emissions of NO_x and VOCs from each member state to the calculated mean April to September ozone concentrations on a 150 km x 150 km grid (Barrettt and Birge, 1996). AOT40 ozone exposures are to be inferred from calculated growing season mean ozone concentrations using an empirical relationship derived from EMEP ozone monitoring network data.

The IIASA/RAINS integrated modelling investigators have constructed a statistical relationship between the long term mean ozone concentrations calculated for each EMEP grid point intersections using the EMEP Photochemical Oxidant model and the country NO_x and VOC emissions (Amann *et al,* 1995). This statistical relationship will then be incorporated into the IIASA/ RAINS integrated assessment model with a view to deriving the least cost combination of country NO_x and VOC emission controls which will allow all ozone critical levels to be reached at least cost. The emission reduction requirements for ozone AOT40 will then be combined with those for acidification and eutrophication, to form an input to the negotiations of the Second NO_x Protocol.

The proposed approach heralds an impressive extension of the integrated assessment tools which have been used to underpin negotiations of Protocols to the UN ECE LRTAP convention. Nevertheless, there are a number of perceived difficulties:

- the spatial scale of the representation of the photochemical oxidant problem is at the country scale. For many European countries this may be too coarse. This has the effect of biasing the control strategies against taking action on VOC emission control in the localised ozone precursor source areas, in favour of NO_x control.
- the approach adopted allows for no change in the tropospheric ozone background concentrations used to initialise the EMEP Photochemical Oxidant model at the start of each trajectory or when boundary layer depths increase and free tropospheric air is intrained into the EMEP model. The emission controls should have an impact on the tropospheric ozone background which should have a strong impact on the growing season mean and AOT40 ozone levels.
- there seems to be no practical method to extend the critical levels approach from a consideration of vegetation damage to a consideration of human health. The adopted approach relies on a large number of trajectories (out of the possible total of 4 per day * 182 days = 728) linking an emission grid square with receptor grid squares over the six months of the growing season. These links will decrease with increasing distance between the emission centroid of the country and the receptor grid-square intersection. This with increasing distance weighting would not be apparent with the worst case trajectory which brought the maximum ozone concentration to each receptor. It is therefore not clear how human health effects can be minimised in the IIASA/RAINS integrated assessment model.

The Working Group on Effects, of the UNECE and the World Health Organisation, sponsored a workshop in Eastbourne in June 1996 to address the question of how to include human health effects from ozone into the integrated assessment modelling (Inst. of Environment and Health, 1996). It has been concluded that a full assessment of health impacts requires more information than that provided by an integration over time of concentration exceeding a defined threshold e.g. AOT40, AOT60, AOT90. It requires the frequency distributions of daily maximum of 8 hour rolling mean ozone concentrations in combination with the size of the population whose potential exposure is described by the respective distribution.

9.3 The Work of the Commission of the European Communities on Ozone

Action on regional scale ozone formation and long range transport is also being undertaken by the Commission of the European Communities. In 1991, the European Communities Ozone Directive was agreed and this sets out various ozone thresholds and the actions to be taken by each member state when they are exceeded. These actions include issuing warnings and alerts to the members of the general public and sending details of exceedances to the Commission. The various threshold levels have been set using the health effects assessments produced by the WHO.

The Commission of the European Communities is also in the process of drafting, consulting upon and promulgating a series of Directives which aim to manage ozone air quality, and to limit or control emissions of ozone precursors. This series of Directives includes an Air Quality Framework Directive and Directives to control motor vehicle exhaust and evaporative emissions, petrol evaporative emissions from oil refineries, petrol distribution and marketing, petrol station forecourts, the painting of motor vehicles and industrial solvent usage. The Commission have instituted an ozone working group to consider and coordinate these actions and strategies. which stem from the implementation of the EC Ozone Directive.

In considering future vehicle emissions from the year 2000 onwards, the Commission of the European Communities has entered into a tripartite evaluation process with the European vehicle and petroleum industries. This process is described in Article 4 of Directive 94/12/EC and is known as the European Auto/Oil programme. It started with a review of the air quality situation currently in the major European cities. Using air quality models, the air quality situation was projected into the future to the years 2000 to 2010 to see if air quality standards were still to be exceeded on current policies. Future proposals developed by the Commission aimed at the improvement of urban air quality are to be based on an understanding of the remaining air quality problems to be resolved, and of the effectiveness and costs of a range of engine, fuel, vehicle inspection and maintenance and traffic management options.

The results of the European Auto/Oil programme are presented for non-reactive pollutants: nitrogen oxides, carbon monoxide and benzene and reactive pollutants: ozone, for a range of cities including: Athens, Den Haag, Koln, London, Lyons, Madrid and Milan. For ozone, the engine options provided for significant reductions in episodic ozone levels calculated with the EMEP photochemical oxidant model. The fuel options produced little change in air quality impacts as indicated by the episodic ozone levels. The Auto/Oil programme recognised that much would need to be done if the European Commission's goal of 90 ppb as the 99th percentile of hourly mean ozone concentration is to be reached in 2010. The EMEP modelling work showed that a 70% reduction in emissions of both NO_x and VOC was needed from both mobile and stationary sources (CONCAWE, 1996).

On the basis of the results of the European Auto/Oil programme, the Commission have drawn up proposals for future exhaust emissions and fuel quality for the year 2000 and beyond. In all discussions, the Commission of the European Communities appears to be entirely concerned with human health impacts and no consideration has been given to effects on crops.

9.4 UK Studies of Policy Options for Photochemical Oxidants

The United Kingdom Department of the Environment, Transport and the Regions has supported research into the assessment of ozone precursor emission control strategies with the UK photochemical trajectory model. Initially, this model studied ozone formation in the London plume (Hough and Derwent, 1987), and then this has been extended with studies of 'worst-case' straight-line trajectories from Germany to Ireland and France to Sweden, (Derwent and Davies, 1994). More recently, real trajectories have been used for six photochemical episode days during 1993 and 1994 to improve the realism with which meteorological processes are represented in the model, (Derwent, 1995). The chemical mechanism and the speciation of the emitted hydrocarbons have been improved steadily over the years and now 69 hydrocarbons from 11 hydrocarbon source categories are included in the model.

The photochemical trajectory model has been used to examine the balance in overall effectiveness between actions to control ozone precursor emissions taken in the United Kingdom alone and those taken in the rest of Europe, excluding the UK. Figure 9.1 shows the impact of curtailing all NO_x and hydrocarbon precursor emissions in the UK only and the rest of Europe only, compared to the base case on this particular photochemical episode day. Action to control ozone precursors in the UK unilaterally appears to result only in small decrease in peak ozone concentrations. Achievement of acceptable ozone air quality in the UK will be dependent on significant action to limit ozone precursor emissions across Europe as a whole. There seems little advantage in the UK developing its own policy outside of that for Europe as a whole (Derwent, 1995).

An important scientific issue concerns where the balance of action should lie between the control of NO_x emissions and hydrocarbon emissions. Figure 9.2 illustrates an approach to answering this question. In this figure each 100 km x 100 km grid square has been assigned to the NO_x or hydrocarbon category depending on whether 50% reduction in that precursor across either the UK or the rest of Europe gives the largest reduction in peak ozone over the base case. In this way, we see that for emission reductions in the rest of Europe, the vast majority of grid squares show a larger reduction following NO_x control rather than hydrocarbon controls. Whereas for controls in the UK alone, hydrocarbon reductions appear to produce the larger reductions in peak ozone concentrations.

These different hydrocarbon and NO_x responses for reductions in local compared with regional scale precursor emissions, are consistent with current understanding of the mechanism of photochemical ozone formation. Ozone is initially formed in the hydrocarbon-limited regime of the intense hydrocarbon and NO_x rich urban and industrial plumes as they spread out from the source regions over downwind distances of the order of 100 km or so. Long range transport takes the ozone once formed to the receptor sites and the chemistry in the NO_x-limited regime merely has to resupply the ozone lost by dry deposition to maintain elevated ozone concentrations over downwind distance scales of up to 1000 km or so.

To take into account the hydrocarbon- and NO_x-limiting regimes, control strategies for episodic ozone need to include both hydrocarbon and NO_x emission reductions. Figure 9.3 summarises the results from a whole series of scenario calculations designed to assess the emission controls required to achieve acceptable air quality with respect to human health in the UK. Depending on the air quality indicator used, reductions in emissions of NO_x and hydrocarbons of 30-90% appear to be required, well beyond those envisaged in current policies.

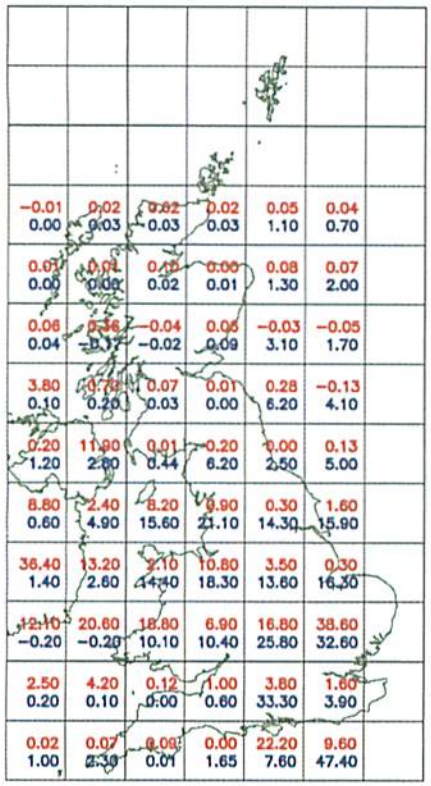
If the EPAQS air quality standard for ozone is not to be exceeded in future years then NO_x and hydrocarbon emission reductions approaching 90% will be necessary across Europe. These reductions approach the limit of economic and technical feasibility (Amann *et al* 1996).

The consideration of the impact of future policies for NO_x and hydrocarbon emission controls on AOT40 values requires a consideration of their impact not only on elevated ozone concentrations during photochemical episodes but also on baseline tropospheric ozone concentrations. Global three-dimensional modelling studies are in hand to examine the impact of reductions in CO, methane, NO_x and hydrocarbon emissions in Europe, Asia and in North America on the tropospheric ozone baseline in Europe (Collins *et al*, 1996).

To illustrate the potential significance of global tropospheric ozone increases driven by growing, future emissions of CH_4 (methane), CO and NO_x throughout the northern hemisphere, the seasonal distribution of surface ozone for European latitudes has been modelled using a two-dimensional chemistry model, TROPOS (Derwent 1996).

TROPOS is a zonally-averaged global chemistry model which has been used to explain how human activities have already led to a doubling in northern hemisphere

A.



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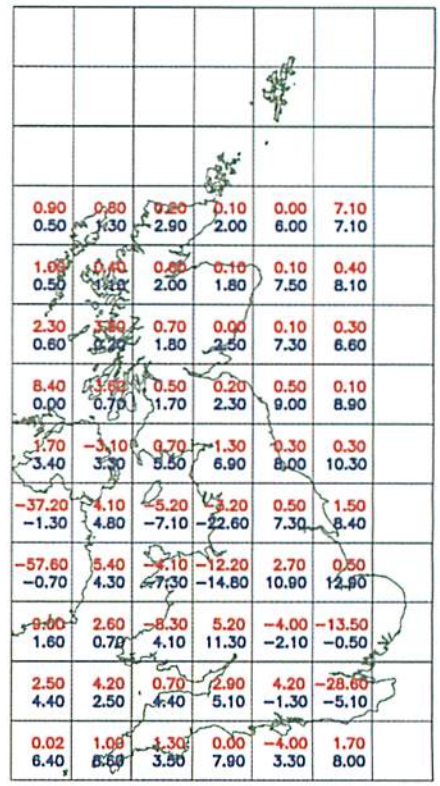
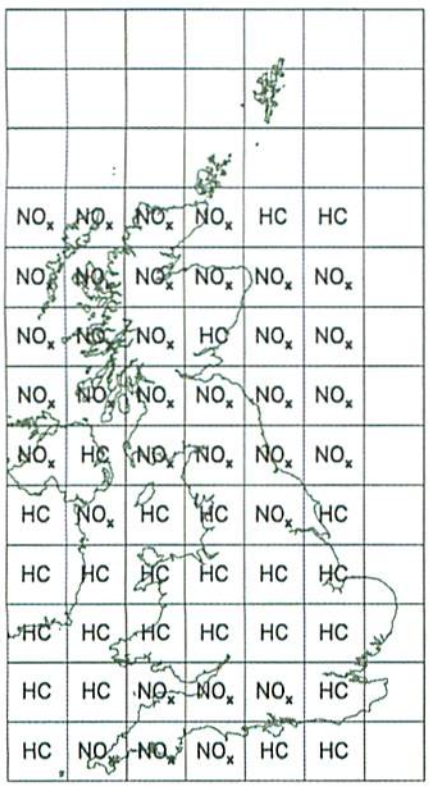


Figure 9.1

A. The decrease in peak ozone concentrations following a 50% reduction in hydrocarbon emissions, showing the comparative impacts of implementing reductions in the UK only (top values) and in the rest of Europe only (bottom values).

B. The decrease in peak ozone concentrations following a 50% reduction in NO_x emissions, showing the comparative impacts of implementing reductions in the UK only (top values) and in the rest of Europe only (bottom values).

A.



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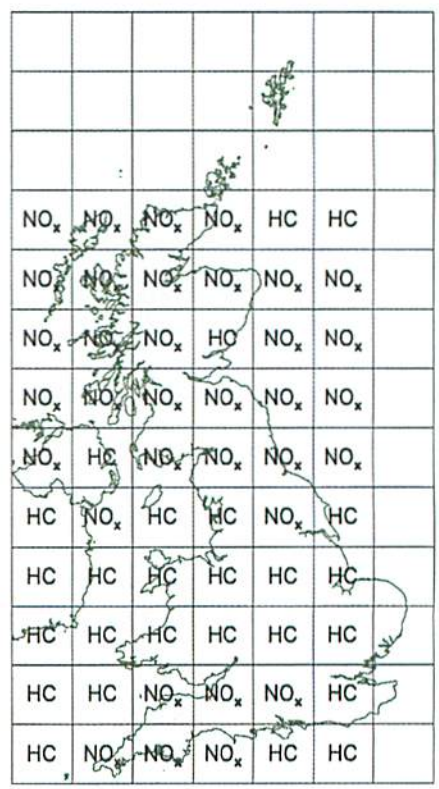

Figure 9.2

A. The categories assigned to each 100 km x 100 km grid square across the UK based on whether ozone formation is hydrocarbon or NO_x limited with respect to emission reductions in the UK only.

B. The categories assigned to each 100 km x 100 km grid square across the UK based on whether ozone formation is hydrocarbon or NO_x limited with respect to emission reductions in Europe only.

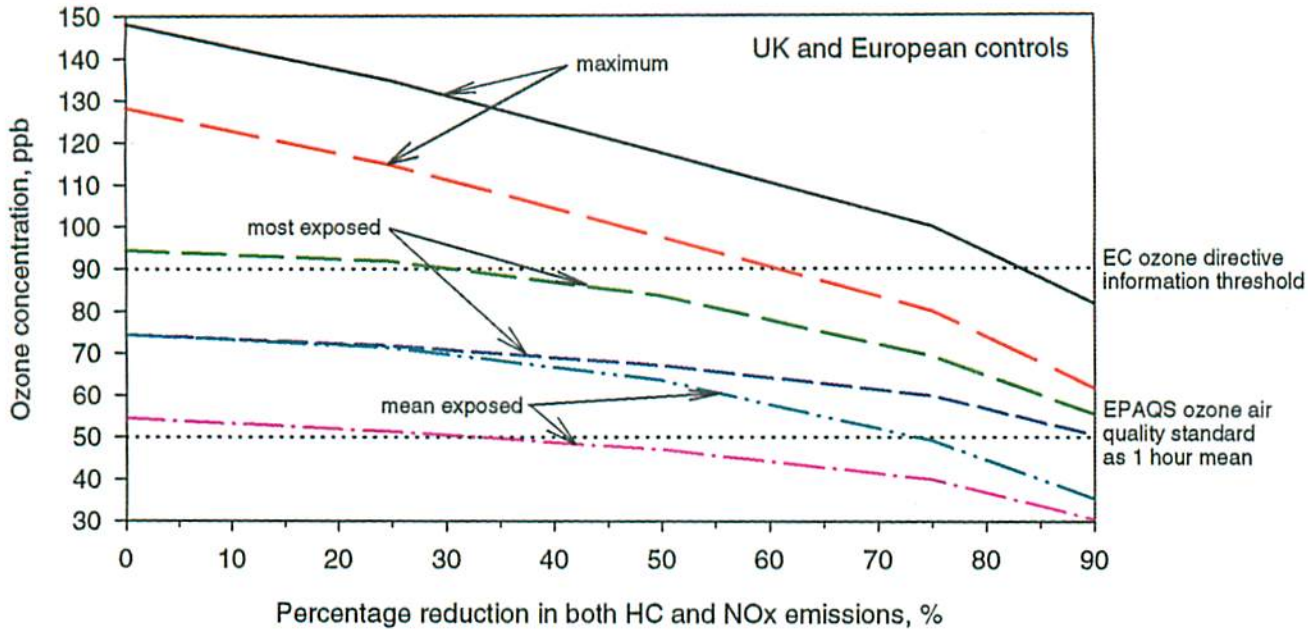

Figure 9.3 Summary of the results of a series of scenario calculations designed to assess the emission controls required to achieve acceptable air quality with respect to human health. 'Maximum' indicates the highest hourly mean ozone concentration experienced within the UK population, 'most exposed' indicates those concentrations experienced by the most exposed 0.5 million of the population and 'mean exposed' the population weighted mean ozone concentration.

ozone background levels since pre-industrial times. Here, TROPOS has been run from 1983 through to the year 2100 using the IS92a scenario of the IPCC (1996) for the assumed emissions of methane, carbon monoxide and nitrogen oxides. Figure 9.4 shows how ozone concentrations are set to increase dramatically through the next century on current projections, thereby increasing AOT40 values throughout Europe and ozone critical levels exceedance.

Current expectations from the TROPOS model in Figure 9.4 are that tropospheric ozone baseline concentrations are expected to rise by about 3.9 ppb during the May to July growing season across the latitude band of Europe over the decade 2000-2010. Figure 9.5a shows that this decadal change implies an increase in AOT40 exposures of about 23-31% at the most exposed UK sites.

This increase in exposure, due to the baseline change, will act to offset any decrease in exposure due to the reduction in severity of regional photochemical episodes. The increase due to the change in baseline could offset a decrease in episodic peak ozone of 24-32% according to Figure 9.5b, equivalent to about one half of the amelioration anticipated by the complete curtailment of NO_x emissions across Europe.

It is therefore of some importance that the global and regional nature of ozone over Europe is fully taken into account in the design of strategies designed to reduce ozone critical levels exceedance and reduce the impact of elevated ozone levels on crops and forest trees.

9.5 Conclusions

There have been significant advances in our understanding of regional scale ozone formation since the publication of our 3rd report, PORG 1993.

- Emission inventories have been developed with some detailed treatments of individual source categories and of hydrocarbon speciation.
- Hydrocarbon monitoring has begun in up to 10 cities in the UK and has allowed a careful check to be made of the accuracy of the emission inventories used in photochemical models.
- Developments in our understanding of the atmospheric chemistry of individual hydrocarbons have allowed the representation of all significant

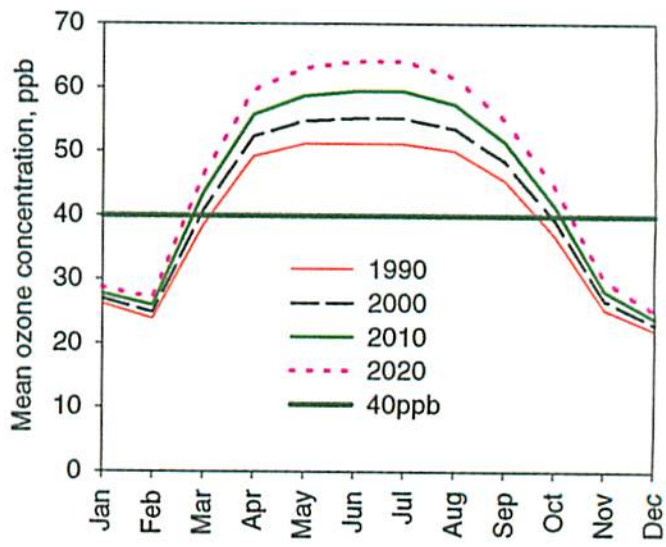

Figure 9.4 TROPOS model results showing how without global scale measures to curb the increasing emissions of greenhouse gases, tropospheric ozone levels will rise through the next century, increasing AOT40 exposures over Europe and hence exceedances of critical levels.

inventoried species in models of episodic ozone formation.

- These models indicate that the relative importance of policy actions to control ozone is strongly weighted in favour of taking action across Europe as a whole and on both hydrocarbon and NO_x emissions.
- If human health based air quality standards are to be met at the level proposed by the Expert Panel on Air Quality Standards then reductions approaching 90% will be required in both NO_x and hydrocarbon emissions across Europe.
- The levels of NO_x and hydrocarbons emission reductions thought to be required to meet challenging health standards are at the limit of those achievable on economic and technical grounds.
- The achievement of ozone critical levels set to protect crops and forest trees will require global scale action on ozone precursor emissions.

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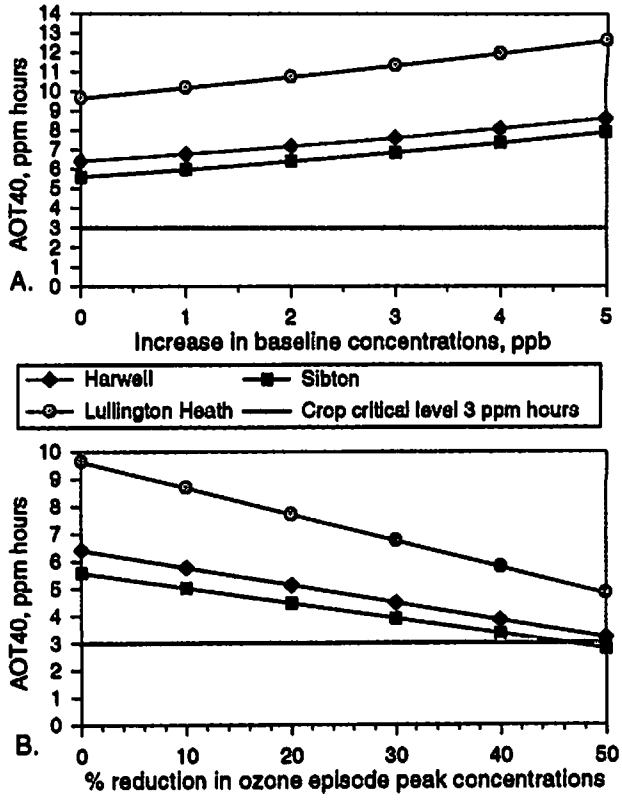

Figure 9.5

A. The influence of increases in baseline (background) ozone concentrations on AOT40 exposure during daylight hours in May to July, 1995, at three rural sites.

B. The influence of reductions in episodic peak ozone concentrations on AOT40 exposure during daylight hours in May to July, 1995, at three rural sites.

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10. RECOMMENDATIONS

The review group in this report has provided a detailed analysis of the ozone climatology of the UK from a limited and very cost effective number of monitoring stations relative to some other European countries. The picture of ground level ozone in the UK is entirely dependent on an adequate monitoring network and in some areas additional monitoring stations are necessary to validate the current maps as indicated below. However, the maintenance and development of the network is essential to underpin any assessment of effects and to detect improvements in air quality as control measures take effect.

A summary of research and monitoring recommendations is provided by the group to maintain and enhance the capability within the UK to quantify exposure and effects of photochemical oxidants and monitor the response of the concentrations to control measures.

Ozone Monitoring

- Maintain the rural network to provide the spatial distribution of ozone in the UK and trends with time. Increase the number of monitoring sites to eliminate large areas of uncertain ozone exposure, notably the East Midlands of England, North and West Wales, the central Highlands of Scotland and inland rural areas of SE England.
- Encourage the development of low cost ozone monitoring techniques, such as solid state sensors and diffusion tube methods.
- Develop further the modelling techniques to quantify the influence of local site factors (land use and shelter).
- Increase the number of stations with co-located rural monitoring of O_3, SO_2, NO, NO_2 and pm10 or pm2.5.
- Quantify the effects of urban areas on ozone climatology to improve estimates of materials and human exposure to the potentially damaging ozone concentrations.
- Provide analysis and interpretation of UK ozone monitoring data for effects assessment and to monitor changes in ambient ozone as precursor emissions decline.
- Develop validated models which describe the small scale spatial variation of ozone within urban and rural areas and its diurnal variation.

NO_x and Chemistry

- Elucidate in detail the composition of NO_y species at UK sites ranging form the most polluted urban centres to the least polluted areas.
- Determine the small scale spatial variations in nitrogen dioxide concentrations within urban areas on a measurement scale of one hour or less.
- Elucidate fully the concentration and formation mechanism of HONO to quantify the role of this compound in the supply of the hydroxyl radical (OH) to the lower atmosphere.
- Assess the extent to which chemical interference in the chemilumiscent method of measurement are influencing the reported concentrations of nitrogen dioxide at UK sites.
- To predict the influence of reductions in nitrogen oxide emissions from road traffic on concentrations of ozone at urban sites.

Hydrocarbons

- To improve understanding of the UK VOC emission it is necessary to attempt closure between the hydrocarbon measurements and emission inventories at a number of key sites and locations.
- Complete an assessment of the contribution made to ozone formation from all emission source categories treated in the National Atmospheric Emissions Inventory.
- Complete spatially disaggregated inventories of the most important individual hydrocarbon emissions so that we can identify those areas in which photochemical oxidant production is under NO_x or hydrocarbon control and whether regionally differentiated strategies for hydrocarbon and NO_x reductions would be more cost effective.
- Investigate the feasibility of identifying those hydrocarbons which are unreactive and make no significant contribution to ozone formation, so that emissions of these species could be deregulated and so that they could be used as substitutes for more reactive hydrocarbons.
- Further research is required to quantify the emission fluxes of reactive oxygenated VOC's from vegetation in the UK and contiguous areas of continental Europe, and to assess the contribution these compounds of biogenic origin make to ozone formation in the region.

Human Health

Additional studies of the following are required:

- The long-term effects of exposure to ambient concentrations of ozone on the incidence of chronic respiratory diseases.
- The interactive effects of exposure to ozone and particulate aerosols, especially acid aerosols and aero-allergens.
- The effects of ozone on other indicators of morbidity such as GP consultations and symptoms.
- The nature of the exposure-response relationship of ozone and whether there is a threshold for population health effects.
- The effects of mixtures of pollutants which include nitrogen dioxide.

- Studies to determine whether ozone has significant effects on health at concentrations of less than 60 ppb (8 hour mean).
- Studies designed to identify those at greatest risk of damage to health on exposure to low concentrations of ozone are needed.

VEGETATION

- It is necessary to quantify the magnitude of yield loss of agricultural crops and forests due to ozone and related photochemical oxidants and its regional variability.
- Quantify exposure of crops and forests to ozone by extending the AOT40 concept to include the flux of absorbed ozone as the measure of dose and develop improved indices of ozone dose to the existing AOT40, which include the uptake of ozone directly.
- Quantify the sensitivity of semi-natural species to ozone and identify likely effects on species composition in natural communities.

MATERIALS

- The current experimentation should be continued to determine those material which are most at risk to damage by ozone.
- Dose-response functions for those materials in applications which are considered to be of economic significance should be developed.
- With the determination of dose-response relationships, a revised economic evaluation should be undertaken of the costs of damage to materials by ozone.
- Effects of changes in the composition of the urban atmosphere should be considered in terms of possible changes in exposure of materials to ozone, allowing a fuller consideration of the economic benefits of emission controls.

SYNTHESIS AND INTERPRETATION

- The current monitoring of urban and rural photochemical oxidants and volatile organic compounds provides an excellent resource for the UK research community. Mechanisms to analyse and interpret these very expensive measurements should be initiated.
- Specifically, the government's air quality strategy for ozone clearly recognises the importance of taking further steps on the European scale to reduce ozone exposure levels. PORG therefore recommends that, in three years time, the government commissions an assessment of:
  - the precursor emission control actions taken across Europe by the year 2000, and their impacts on ambient NO_x and hydrocarbon concentrations,
  - the resulting change in ozone exposure levels and their likely impact on human health and damage to vegetation,
  - the requirement for and timing of additional policy actions to control hydrocarbons and NO_x across Europe, and their likely impact over the period upto 2010.

LIST OF FIGURES

LIST OF TABLES

APPENDIX 1: MEMBERSHIP, ACKNOWLEDGEMENTS AND TERMS OF REFERENCE

MEMBERSHIP

Prof. D. Fowler (Chairman)
Institute of Terrestrial Ecology
Edinburgh Research Station
Bush Estate
Penicuik
Midlothian, EH26 0QB
Tel. 0131 445 8535 / 4343
Fax. 0131 445 3943
Email David.Fowler@ite.ac.uk

Ms. M. Coyle (Secretary and Editor)
Institute of Terrestrial Ecology
Edinburgh Research Station
Bush Estate
Penicuik
Midlothian, EH26 0QB
Tel. 0131 445 8518 / 4343
Fax. 0131 445 3943
Email Mhairi.L.Coyle@ite.ac.uk

Prof. R. Anderson
Dept. of Public Health Sciences
St George's Hospital Medical School
Cranmer Terrace
London, SW17 ORE
Tel (recp) 0181 672 9944
(direct) 0181 725 9944
Fax 0181 725 3584
Email randerso@sghms.ac.uk

Dr. M.R. Ashmore
Centre for Environmental Technology
Imperial College of Science, Technology and Medicine
48 Princes Gardens
London, SW7 2PE
Tel. 0171 594 9291
Fax. 0171 581 0245
Email: m.ashmore@ic.ac.uk

Dr J.S. Bower
AEA Technology
National Environmental Technology Centre
Culham, Abingdon
Oxfordshire, OX14 3DB
Tel. 01235 463 067
Fax. 01235 463 005
Email: jon.bower@aeat.co.uk
jean.theobold@aeat.co.uk

Ms R.A. Burgess
School of Environmental Sciences
University of East Anglia
Norwich, NR4 7TJ
Tel. 01603 592532 / 592016
Fax. 01603 507719 / 452 420
Email: r.a.burgess@uea.ac.uk

Dr. J.N. Cape
Institute of Terrestrial Ecology
Edinburgh Research Station
Bush Estate
Penicuik
Midlothian, EH26 0QB
Tel. 0131 445 8533 / 4343
Fax. 0131 445 3943
Email J-Neil.N.Cape@ite.ac.uk

Dr. R.A. Cox
Centre for Atmospheric Science
Department of Chemistry
University of Cambridge
Lensfield Road
Cambridge, CB2 1EP
Tel. 01223 336253 / 336487
Fax: 01223 336362
Email: rac26@cam.ac.uk

Dr. R.G. Derwent
Room 156
Met O (APR)
Meteorological Office
London Road
Bracknell
Berks, RG12 2SY
Tel. 01344 854624
Fax. 01344 854493
Email: rgderwent@meto.govt.uk

Dr. G.J. Dollard
AEA Technology
National Environmental Technology Centre
Culham
Abingdon
Oxon, OX11 0RA
Tel. 01235 463 094 / 114
Fax. 01235 463 005
Email: geoff.dollard@aeat.co.uk
yoland.jackson@aeat.co.uk

Prof. P. Grennfelt
Swedish Institute of Environmental Research (IVL)
PO Box 47086
S - 40258
Gothenburg, Sweden
Tel +46 31 46 00 80
Fax +46 31 48 21 80
Email grennfelt@ivl.se

Prof. R.M. Harrison
School of Chemistry
University of Birmingham
Edgebaston
Birmingham, B15 2TT
Tel. 0121 414 3493
Fax. 0121 414 3709
Email r.m.harrison.ipe@bham.ac.uk

Prof. C.N. Hewitt
Division of Environmental Sciences
Institute of Environmental and Biological Sciences
Lancaster University
Lancaster, LA1 4YQ
Tel. 01524 593931
Fax. 01524 843854
Email: n.hewitt@lancaster.ac.uk

Prof. Ø. Hov
The Norwegian Institute of Air Research (NILU)
Instituttveien 18
PO Box 100
N-2007 Kjeller
Norway
Tel 00 47 (55) 212636
Fax 00 47 (55) 960566

Dr M.E. Jenkin
AEA Technology
National Environmental Technology Centre
Culham, Abingdon
Oxfordshire, OX14 3DB
Tel. 01235 463 118
Fax. 01235 463005
Email: michael.e.jenkin@aeat.co.uk

Dr D.S. Lee
AEA Technology
National Environmental Technology Centre
Culham, Abingdon
Oxon, OX14 0RA
Tel. 01235 463 130
Fax. 01235 463 005
Email: david.s.lee@aeat.co.uk

Dr R.L. Maynard
Department of Health
Room 658C
Skipton House
80 London Road
London, SE1 6LW
Tel. 0171 972 5118 / 5115
Fax. 0171 972 5167

Prof. S.A. Penkett
School of Environmental Sciences
University of East Anglia
Norwich, NR4 7TJ
Tel. 01603 592532 / 592016
Fax. 01603 507719 / 452 420
Email: m.penkett@uea.ac.uk

Mr. R.I. Smith
Institute of Terrestrial Ecology
Edinburgh Research Station
Bush Estate
Penicuik
Midlothian, EH26 0QB
Tel. 0131 445 8505 / 4343
Fax. 0131 445 3943
Email Rognvald.I.Smith@ite.ac.uk

J.R. Stedman
AEA Technology
National Environmental Technology Centre
Culham, Abingdon
Oxfordshire, OX14 3DB
Tel 01235 463 178
Fax. 01235 463 817
Email: john.stedman@aeat.co.uk

Dr K.J. Weston
Department of Meteorology
University of Edinburgh
Kings Buildings
Mayfield Road
Edinburgh, EH9 3JZ
Tel. 0131 650 5093
Fax. 0131 662 4269
Email: kjw@met.ed.ac.uk

Dr M.L. Williams
Department of the Environment
Room B356
Romney House
43 Marsham Street
London, SW1P 3PY
Tel. 0171 276 8881
Fax. 0171 276 8821
Email: martin.williams.aeq@dial.pipex.com

Dr P.J. Woods
Quantum Meteorological Division
National Physical Laboratory
Teddington
Middlesex, TW11 0LW
Tel. 0181 943 70955
Fax. 0181 943 675
Email: ptw2@newton.npl.co.uk

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Geoff Broughton
AEA Technology, National Environmental Technology Centre

Helen M. Dyke
Institute of Terrestrial Ecology, Monks Wood Experimental Station

Justin Goodwin
AEA Technology, National Environmental Technology Centre

Anne-Gunne Hjellbrekke
The Norwegian Institute of Air Research (NILU)

Dr Martin J.T Milton
Quantum Meteorological Division, National Physical Laboratory

Dr Roger H. Partridge
Quantum Meteorological Division, National Physical Laboratory

Dr. Carole Pitcairn
Institute of Terrestrial Ecology, Edinburgh Research Station

Mr Robert Storeton-West
Institute of Terrestrial Ecology, Edinburgh Research Station

Mr Bryan P. Sweeney
Quantum Meteorological Division, National Physical Laboratory

PHOTOCHEMICAL OXIDANTS REVIEW GROUP – TERMS OF REFERENCE

1. The Photochemical Oxidants Review Group is an official body of experts set up by the Department of the Environment to review current knowledge on the physical and chemical aspects of photochemical oxidants and associated precursors. It is a working body and not just a liaison group.

2. The initial goal was to prepare a preliminary review of the photochemical oxidant climate of the United Kingdom, published in February 1987. This was followed by; a review of nitrogen oxides in the United Kingdom in 1990; ozone and nitrogen dioxides in 1993; ozone, nitrogen oxides and volatile organic compounds in 1997.

3. In preparing the above reviews, the group has identified critical areas of uncertainty and recommended where further research, within the overall national effort, is needed.

4. The group makes recommendations for changes to relevant monitoring networks in the United Kingdom.

5. The group provides an informal forum for discussion of research plans and results.

6. The Group acts as a point of liaison with relevant international bodies.

APPENDIX 2: UK AIR QUALITY MEASUREMENT SITES AND INFORMATION SOURCES (1/7/96)

Full Name	Site Ref	Class	OS Grid Ref	Altitude, m (±10m)	Network/ Operator	O_3 in PORG Database	O_3	NO_x	CO	SO_2	pm10	HC	Measurement Period
Aston Hill	AH	R	SO298901	370	ARN	Y	✓	-	-	-	-	-	26/06/86 ~
On the summit of a hill with clear views of surrounding arable farmland.													
Ascot	AS	R	SU946688	65	IC	Y	✓	-	-	-	-	-	1979 - 1984
In grounds of research establishment in a rural area.													
St. Bartholomew's	BA	U	TQ319821	15	MRC	Y	✓	-	-	-	-	-	1976 - 1976
Adjacent to small square, mixed commercial/residential, ~50m from busy road.													
Belfast Centre	BC	UC	J339744	-	AUN	N	✓	✓	✓	✓	✓	-	08/03/92 ~
Pedestrianised street (Lombard St) 25 m from major road.													
Belfast East	BE	UB	J357740	20	AUN	N	-	-	-	✓	-	-	06/09/89 ~
Situated in a first floor room of a recreation centre in a residential district of Belfast.													
Belfast South	BF	UB	J333726	-	HCN	N	-	-	-	-	-	✓	23/08/93 ~
Situated 10m to the rear of a row of terraced houses in College Gardens. 100m west of a major road.													
Birmingham Centre	BH	UC	SP064868	135	AUN	N	✓	✓	✓	✓	✓		18/03/92 ~
Pedestrianised area (Centenary Square), 100 m from major road; 10 m from small car park.													
Bircotes	BI	U	SK629922	30	WSL	N	-	-	-	✓	-	-	14/09/89 - 11/03/91
A residential area - 1 km north of a colliery and 2 km west of the A1(M).													
Birmingham Kerb	BK	UK	SP070870	130	WSL	N	-	-	✓	-	-	-	13/03/74 - 7/01/78
On the kerbside of Stratford Road with 1:20 gradient and 20,000 vehicles per day.													
Bristol East	BL	UB	ST599729	5	HCN	N	-	-	-	-	-	✓	01/04/94 ~
Situated in the South East corner of the grounds of the Hannah More Primary School, Jubilee Street.													
Billingham	BM	UI	NZ470237	10	AUN	N	-	✓	-	-	-	-	01/01/87 ~
Residential area. A council depot with a large complex of chemical / manufacturing plant 1-3 km to the south.													
Barnsley	BN	U	SE348094	90	WSL	N	-	-	-	✓	-	-	14/03/91 - 21/03/94
Municipal building on edge of a coal mining town.													
Bristol Centre	BO	UC	ST594732	10	AUN	N	✓	✓	✓	✓	✓	-	04/01/93 ~
Pedestrianised walkway (Lower Castle Street to Bond Street), 43 m from major road.													
Bridge Place	BP	UB	TQ291790	20	AUN	Y	✓	✓	✓	✓	-	-	03/07/90 ~
Office overlooking backstreet near Victoria Station, replaced Central London in 1991.													
Brampton	BR	R	SK843810	6	PG	Y	✓	-	-	-	-	-	1981 - 1985
3km ENE of Cottam power station, 100m E of A156.													
Birmingham East*	BS	UB	SP116889	105	AUN/HCN	N	✓	✓	✓	✓	✓	✓	23/08/93 ~
Within playground of a Junior and Infant School in a residential area.													
Bottesford	BT	R	SK797376	32	ARN	Y	✓	-	-	-	-	-	01/10/77 ~
1 km from Bottesford village on open farmland.1 km south of A52.													
Bush	BU	R	NT245635	180	ARN	Y	✓	✓	-	✓	-	-	01/04/86 ~
On a flat plain between hills. Site surrounded by open and forested land. ITE buildings nearby.													
Barnsley 12	BY	U	SE342067	100	AUN	N	-	-	-	✓	-	-	21/03/94 ~
Municipal building in centre of a coal mining town. 200 m from an arterial road													
Cardiff Centre	CC	UC	ST184765	10	AUN	N	✓	✓	✓	✓	✓	-	12/05/92 ~
Pedestrianised street (Frederick Street) 190 m from major road.													
Cardiff East	CF	UB	ST193773	10	HCN	N	-	-	-	-	-	✓	01/11/93 ~
Situated off Croft Street in the Roath District of Cardiff.													
Chigwell	CG	U	TQ442919	52	TBV	Y	✓	-	-	-	-	-	1979, 1982-1985
Outer London, in garden of residential area.													
County Hall	CH	U	TQ306797	27	TBV	Y	✓	-	-	-	-	-	1975-76, 1978-1986, 1989
Rooftops of central London.													

Full Name	Site Ref	Class	OS Grid Ref	Altitude, m (±10m)	Network/ Operator	O_3 in PORG Database	O_3	NO_x	CO	SO_2	pm10	HC	Measurement Period
Cardiff Kerbside	CK	UK	ST183766	10	WSL	Y	✓	-	✓	-	-	-	28/07/73 - 23/11/76
Kerbside of the busy Queen Street with 30,000 vehicles per day, 1974 O3 data is in the PORG data base with site reference CD.													
Central London	CL	UC	TQ292791	20	WSL	Y	✓	✓	✓	✓	-	-	01/07/72 - 20/08/90
Situated facing a quiet street, located in Victoria..													
Cambridge	CM	UK	TL450580	10	WSL	N	-	-	✓	-	-	-	01/11/74 - 01/03/78
Busy kerbside on Bridge Street which is a narrow road with 7,000 vehicles per day.													
London Camden*	CN	UK	TQ267843	55	AUN	N	-	✓	-	-	✓	-	16/05/96 ~
Roadside site in Camden.													
Cromwell Road	CR	UK	TQ264789	20	AUN	Y	✓	✓	✓	✓	-	-	22/02/73 ~
Located at the kerbside of a busy arterial road in Central London. Traffic density approx. 60,000 vehicles per day. O_3 measured in 1973 and 1974													
Clatteringshaws	CT	R	NX553779	180	NPTEC	Y	✓	-	-	-	-	-	1986 - 1990
Canvey Island	CV	SU	TQ782847	3	WSL	Y	✓	✓	✓	-	-	-	10/05/77 - 01/10/80
On open flat countryside on Canvey Island. Approximately 2 km from the oil refinery and methane terminal.													
Chilworth	CW	SU	SU405183	80	WSL	Y	✓	-	-	-	-	-	18/04/75 - 10/10/75
Rural site in the new forest.													
Devilla	DE	R	NS957894	80	ITE	Y	✓	-	-	-	-	-	1977 - 1980
Forest area, sampling 2m above top of canopy.													
Dunslair Heights	DH	R	NT280430	600	ITE	Y	✓	-	-	-	-	-	13/06/92 ~
On open hilltop, surrounded by forestry plantation.													
Dursley	DR	R	ST755967	160	NPTEC	Y	✓	-	-	-	-	-	1987 - 1990
Edinburgh Centre	ED	UC	NT254738	60	AUN	N	✓	✓	✓	✓	✓	-	04/10/92 ~
Urban parkland (E. Princes St. Gardens), 35 m from major road, overlooking Waverley train station.													
Edinburgh Med. School	EH	UB	NT257730	60	HCN	N	-	-	-	-	-	✓	27/08/93 ~
Situated in the Medical School of Edinburgh University.													
East Kilbride	EK	SU	NS638534	50	WSL	Y	✓	-	-	-	-	-	08/05/75 - 09/10/75
Open area in new town.													
East Malling	EM	R	TQ712572	32	TBV	Y	✓	-	-	-	-	-	1984 - 1985
Outer London, agricultural /residential area.													
Eskdalemuir	ES	R	NT235028	269	ARN	Y	✓	-	-	-	-	-	23/04/86 ~
Situated on open moorland adjacent (500m) to Met Office Laboratory.													
Fawley	FL	U	SU474202	30	NPTEC	Y	✓	-	-	-	-	-	1988 - 1991
Featherstone	FS	U	SE429195	50	WSL	N	-	-	-	✓	-	-	14/09/89 - 13/03/91
A residential area - 1 km south of a colliery.													
Great Dun Fell	GD	RR	NY711322	847	ARN	Y	✓	-	-	-	-	-	09/05/86 ~
Near mountain summit and often above the cloud base.													
Glasgow Hope St	GH	UK	NS587651	35	WSL	N	-	✓	✓	✓	-	-	27/06/73 - 28/10/82
Kerbside of Hope Street which is a busy road, large percentage of diesel traffic.													
Glasgow	GL	U	NS554678	40	ITE	Y	✓	-	-	-	-	-	1983 - 1987
Great Western Rd.													
Glasgow	GW	UB	NS595653	90	AUN	N	-	✓	✓	-	-	-	06/01/87 ~
Central city near-kerbside location (8m from road). Partially residential area, but with large traffic volumes in surrounding areas.													
Glazebury	GZ	R	SJ690959	21	ARN	Y	✓	-	-	-	-	-	1/4/88 ~
On open, flat, ground in horticultural area between conurbations.													
London, Haringey 1*	HA	UK	TQ339906	15	AUN	N	-	✓	-	-	✓	-	16/05/96 ~
Local authority affiliated site.													
London, Haringey 2*	HB	UC	TQ339907	15	AUN	N	✓	-	-	-	-	-	16/05/96 ~
Local authority affiliated site.													
High Muffles	HM	R	SE776939	267	ARN	Y	✓	-	-	-	-	-	16/07/87 ~
Hilly moorland and forestry plantation.													

Full Name	Site Ref	Class	OS Grid Ref	Altitude, m (±10m)	Network/ Operator	O_3 in PORG Database	O_3	NO_x	CO	SO_2	pm10	HC	Measurement Period
Hainault Outer London, adjacent to a park in a residential area.	HN	U	TQ460917	44	TBV	Y	✓	-	-	-	-	-	1974 - 1975
Harrow Situated in the grounds of the High School. Predominantly residential suburban area of North West London, with some light industrial and commercial activity.	HO	SU	TQ143874	60	WSL	Y	✓	✓	-	-	-	-	30/07/79 - 03/10/80
Harwell Harwell research laboratories which is surrounded by flat cereal fields. The busy A34 is nearby.	HR	R	SU474863	137	AUN/HCN	Y	✓	✓	-	✓	-	✓	22/06/76 ~
Hull Centre Open area on the edge of Queen's Gardens, near Vernon Street.	HU	UC	TA097288	1	AUN	N	✓	✓	✓	✓	✓	-	04/01/94 ~
Hazelrigg	HZ	R	SD492579	91	LANC.U	Y	✓	-	-	-	-	-	1981 - 1982
Islington Commercial, inner city area on Wharf Road.	IS	U	TQ321831	20	WSL	Y	✓	✓	-	-	-	-	09/07/76 - 11/10/78
Jenny Hurn 8km north of Gainsborough.	JH	R	SK817986	4	PG	Y	✓	-	-	-	-	-	1984 - 1988
London, Kensington & Chelsea 1* Local authority affiliated site.	KC	UB	TQ401821	10	AUN	N	✓	✓	✓	✓	✓	-	1996 ~
Kew Garden in suburban area.	KW	U	TQ185779	10	IC	Y	✓	-	-	-	-	-	1978
London, Sutton 1* Local authority affiliated site.	LA	UK	TQ256646	50	AUN	N	-	✓	✓	✓	✓	-	1/4/96 ~
Ladybower Adjacent to forested area overlooking reservoir in Peak National Park.	LB	R	SK164892	420	ARN	Y	✓	✓	-	✓	-	-	15/07/88 ~
Leicester Centre Pedestrianised area at New Walk Centre, Welford Place.	LC	UC	SK587040	65	AUN	N	✓	✓	✓	✓	✓	-	04/01/94 ~
Leeds Centre Open area (Queens Square Court) 30 m from major road.	LD	UC	SE299343	60	AUN	N	✓	✓	✓	✓	✓	-	04/01/93 ~
London Eltham* Situated near a golf course and school, on the north side of Bexley Road.	LE	SU	TQ440747	50	AUN/HCN	N	✓	✓	-	✓	✓	✓	04/03/93 ~
Lullington Heath On a high plateau 5 km from the south coast. Immediate area is a NCC heathland.	LH	R	TQ538016	120	ARN	Y	✓	✓	-	✓	-	-	04/10/86 ~
London, Tower Hamlets 2* Local authority affiliated site.	LM	UK	TQ521816	5	AUN	N	-	✓	✓	-	-	-	01/04/96 ~
Lincoln 100m from roads, 70m from houses.	LN	U	SK983729	54	PG	Y	✓	-	-	-	-	-	1986 - 1988
London, Sutton 3* Local authority affiliated site.	LO	SU	TQ278548	160	AUN	N	✓	✓	-	-	-	-	1/4/96 ~
Leeds Potternewton Situated in the grounds of Leeds Environment Department, Blake Grove.	LP	UB	SE307367	90	HCN	N	-	-	-	-	-	✓	13/01/95 ~
Lough Navar Clearing within a forestry plantation.	LR	RR	IH065545	130	ARN	Y	✓	-	-	-	✓	-	02/04/87 ~
Liverpool Speke Situated in the North East corner of the grounds of St Christophers Primary School, Tarbock Road.	LS	UB	SJ438835	30	HCN	N	-	-	-	-	-	✓	01/12/95 ~
London Brent*	LT	UB	TQ200840	40	AUN	N	✓	✓	✓	✓	✓	-	26/01/96 ~
London, UCL or Bloomsbury Situated in the Department of Geography, University College London, very close to the London Bloomsbury site, LY.	LU	UK	TQ299822	25	HCN	N	-	-	-	-	-	✓	11/02/93 ~
London, Wandsworth 2* Local authority affiliated site.	LW	UC	TQ264746	25	AUN	N	✓	✓	-	-	-	-	1/4/96 ~
London Bexley* Community centre car park off Bridge Rd in residential area.	LX	SU	TQ518763	25	AUN	N	✓	✓	✓	✓	✓	-	01/05/94 ~

Full Name	Site Ref	Class	OS Grid Ref	Altitude, m (±10m)	Network/ Operator	O_3 in PORG Database	O_3	NO_x	CO	SO_2	pm10	HC	Measurement Period
Liverpool Centre City centre municipal gardens.	LV	UC	SJ349908	15	AUN	N	✓	✓	✓	✓	✓	-	23/04/93 ~
London Bloomsbury Land at Russell Square Gardens (south-east quadrant). 35 m from kerbside.	LY	UC	TQ302820	25	AUN	N	✓	✓	✓	✓	✓	-	23/01/92 ~
Middlesbrough* Situated in a residential area near Longlands College of Further Education.	MD	UI	NZ505194	10	AUN/HCN	N	✓	✓	✓	✓	✓	✓	01/01/93 ~
Mace Head Remote open flat land on Atlantic coast.	MH	RR	IL740320	15	UBRIS	Y	✓	-	-	-	-	-	09/06/87 ~
Manchester Piccadilly Located in Piccadilly Gardens in busy city centre. 20m from the nearest road.	MP	UC	SJ843983	35	AUN	N	✓	✓	✓	✓	✓	-	18/12/95 ~
Manchester Town Hall City centre but elevated location. 20 m from nearest road, 150 m from large thoroughfare (St Peter's Square).	MT	UB	SJ838980	35	AUN	N	-	✓	✓	-	-	-	22/01/87 ~
Newcastle Centre Located in St Mary's Place Car Park near the Civic Centre. (Mar92-June94 North side of Princess Square, 40 m from road.)	NC	UC	NZ251649	25	AUN	N	✓	✓	✓	✓	✓	-	08/03/92 ~
North Norfolk Coastal site.	NN	R	TG141388	98	UEA	Y	✓	-	-	-	-	-	1989 - 1990
Nat West Tower Central London high up on tower.	NW	U	TQ331814	204	TBV	Y	✓	-	-	-	-	-	1983
Oxford Centre* Situated 3m above the pavement of St Aldate's which is a busy shopping Street.	OC	UK	SP514092	60	AUN	N	-	✓	✓	✓	-	-	15/04/96 ~
Rochester* North corner of playing field in Lower Stoke village primary school. 90m from buildings, 100m from residential street on the rural Isle of Grain.	RO	R	TQ831762	10	ARN	N	✓	✓	-	✓	✓	-	26/01/96 ~
Rugeley Municipal building on edge of small town.	RU	UB	SK043173	90	WSL	N	-	-	-	✓	-	-	21/03/91 - 17/09/92
Sibton Open flat cereal farmland. Woodland to the north west.	SB	R	TM364719	46	ARN	Y	✓	✓	-	✓	-	-	01/07/73 ~
Sheffield Centre Located at the junction of Charter Row and Furnival Gate. 30m from road with 20,000 cars per day.	SC	UC	SK352869	85	AUN	N	✓	✓	✓	✓	✓	-	01/01/96 ~
Stodday	SD	R	SD462587	10	LANC.U	Y	✓	-	-	-	-	-	1982 - 1984
Southampton Centre Open grassy area at junction between Brinton's Road and Northam Road.	SH	UC	SU440130	10	AUN/HCN	N	✓	✓	✓	✓	✓	✓	04/01/94 ~
Sheffield Tinsley Near community centre in a mixed residential /industrial area 200 m from the M1.	SL	UI	SK402906	90	AUN	N	-	✓	✓	-	-	-	28/11/90 ~
St. Osyth	SO	R	TM104183	5	U.ESSX	Y	✓	-	-	-	-	-	1985 - 1987
Somerton* Located at Somerton Radio Station at the summit of a hill. In open pasture with minor roads 2km south of Somerton.	SS	R	ST486268	55	ARN	N	✓	-	-	-	-	-	26/01/96 ~
Stevenage On the edge of a residential new town near a light industrial estate. 100 m east of A1(M) motorway. Topography flat. Formerly an ARN site.	ST	SU	TL237225	90	WSL	Y	✓	✓	✓	✓	✓	-	22/06/76 - 29/04/94
Sunderland Commercial and residential with river and port industries from north west and east.	SU	UB	NZ398570	33	AUN	N	-	-	-	✓	-	-	06/10/92 ~
Strath Vaich Remote hilly moorland, used for sheep-grazing.	SV	RR	NH347750	270	ARN	Y	✓	✓	-	✓	-	-	18/03/87 ~
Swansea* Pedestrianised area of Princess Way in city centre.	SW	UC	SS655931	25	AUN	N	✓	✓	✓	✓	✓	-	01/12/94 ~
Syda House Holymoor, 7km west of Chesterfield.	SY	R	SK312696	308	PG	Y	✓	-	-	-	-	-	1986 - 1988
Teddington Close to parkland, 20m above the ground, within the NPL building complex.	TD	SU	TQ156706	20	NPL	Y	✓	-	-	-	-	-	1975-76, 1978, 1982-1985, 1987-1991
Teddington* Close to parkland within NPL building complex.	TN	SU	TQ150700	20	ARN	N	✓	✓	-	✓	-	-	20/08/96 ~

Full Name	Site Ref	Class	OS Grid Ref	Altitude, m (±10m)	Network/ Operator	O_3 in PORG Database	O_3	NO_x	CO	SO_2	pm10	HC	Measurement Period
Thorney	TH	R	SK858731	8	PG	Y	✓	-	-	-	-	-	1981 - 1988
5.4km ENE of High Marnham power station.													
West Burton	WB	R	SK804864	4	PG	Y	✓	-	-	-	-	-	1981 - 1984
1.4km ENE West Burton of power station.													
Wharleycroft	WC	R	NY698247	206	ARN	Y	✓	-	-	-	-	-	08/05/85 - 28/11/95
Within valley at the base of Great Dun Fell.													
West London	WL	UB	TQ251788	20	AUN	N	-	✓	✓	-	-	-	01/01/87 ~
Located in a municipal depot in a partially residential area bounded on all sides by major roads. 90 m from Warwick Road.													
Wray	WR	R	SD619678	100	WSL	Y	✓	-	-	-	-	-	01/04/85 - 29/02/88
Farmyard location in rural hilly area.													
Walsall	WS	UB	SO994982	20	AUN	N	-	✓	-	-	-	-	05/03/87 ~
A school site 200 m to the west of the M6 (traffic flow approx. 70,000 vehicles per day). Residential area with metal smelting plant 500m to the south.													
Wolverhampton Centre	WV	UC	SO914989	150	AUN	N	✓	✓	✓	✓	✓	-	18/12/95 ~
Located on the edge of a car park in St Peter's Square. Next to a busy pedestrian walk way and 30m from the city ring road.													
Weybourne	WY	R	TG110430	10	UEA	Y	✓	-	-	-	-	-	01/01/95 ~
Close to beach on North coast of Norfolk.													
Yorkminster	YK	U	SE603522	50	PG	Y	✓	-	-	-	-	-	1986 - 1990
Rooftop of cathedral, in chamber under central tower.													
Yarner Wood	YW	R	SX786789	119	ARN	Y	✓	-	-	-	-	-	26/06/87 ~
Undulating moorland with semi-natural broad-leaved woodland.													

Classes

RR	remote rural
R	rural
SU	sub-urban
U	general urban (sites in the PORG database)
UC	urban centre
UB	urban background
UK	urban kerbside/roadside
UI	urban industrial

Other Information

+ Local authority affiliated site, set up with the advice and support of AEAT, NETCEN.
* not operational as of 1/7/96

Network/Operator

ARN	Automatic Rural Network
AUN	Automatic Urban Network
HCN	HydroCarbon Network
IC	Imperial College, London
MRC	Medical Research Council
WSL	Warren Spring Laboratory (now part of AEAT, NETCEN)
PG	Powergen
TBV	TBV Science
NPTEC	National Power and Technology
ITE	Institute of Terrestrial Ecology
LANC.U	Lancaster University, Dept. of Environmental Sciences
UBRIS	University of Bristol, Dept. of Biogeochemistry
U.ESSX	University of Essex
NPL	National Physical Laboratory
UEA	University of East Anglia, School of Environmental Science

Details of air quality information sources.

Air Quality Monitoring Information Over the Phone

The Department of the Environment, Transport and the Regions has a freephone number for hourly updated recorded bulletins:

0800 55 66 77

Air Quality Monitoring Data and Information on the World Wide Web

The home page for all the UK air quality monitoring information can be found at WWW address:

http://www.aeat.co.uk/products/centres/netcen/airqual/welcome.html

From here several pages can be accessed :

Air Quality Bulletins
Air Quality Monitoring Networks
Air Quality Forecasting
Acid Deposition Information
National Atmospheric Emissions Inventory
Chemistry of Atmospheric Pollutants

Archive data can be viewed and downloaded from WWW pages:

http://www.aeat.co.uk/products/centres/netcen/aqarchive/archome.html

Air Quality Monitoring Data and Information on Ceefax and Teletext

Title	Ceefax page	Teletext page
Air Quality Information (main index)	**410**	**106**
General UK Forecast	411	
Wales, Scotland and Northern Ireland	412	
North England	413	
Central England	414	
South England	415	

APPENDIX 3: UNITS AND CONVERSION FACTORS

UNITS OF CONCENTRATION MEASUREMENT

The expression of air pollutant concentrations in more than one unit of measurement can cause confusion for those not professionally involved in the field. There are two main systems of unit in common use:

1. Mass per unit volume: usually μg m^{-3}. The mass of pollutant is expressed as a ratio to the volume of air. Since the volume of a given parcel of air is dependent upon the temperature and pressure at the time of sampling, the pollutant concentration expressed in these units should, strictly speaking, specify the conditions at the time of sampling.
2. Volume mixing ratio: usually ppm - parts per million (10^6); or ppb - parts per billion (10^9); or ppt - parts per trillion (10^{12}). This unit expressed the concentration of a pollutant as the ratio of its volume if segregated pure, to the volume of the air in which it is contained. Ideal gas behaviour is assumed and thus the concentration is not dependent upon temperature and pressure as these affect both the pollutant and the air to the same extent. As a consequence of the gas laws, a gas present at a volume mixing ratio of 1 ppm is not only 1 cm^3 per 10^6 cm^3 of polluted air, it is also 1 molecule per 10^6 molecules and has a partial pressure of one millionth of the atmospheric pressure.

Some pollutants (e.g. sulphate, nitrate) are present as particles in the air and the concept of a volume mixing ratio of gases is not obviously applicable. Their concentrations are normally expressed only in μg m^{-3} units.

CONVERSION FACTORS

Interconversion of the two sets of units can be achieved as follows:

$$\frac{\mu g\ m^{-3}}{1000} = \frac{\text{ppb x molecular weight (grammes)}}{\text{molecular volume (litres)}}$$

where, $$\text{molecular volume} = 22.41 \times \frac{T}{273} \times \frac{1013}{P} \text{ litres}$$

in which T = absolute temperature (K)

P = atmospheric pressure (mb)

Similarly,

$$\text{ppb} = \frac{\mu g\ m^{-3}}{1000} \times \frac{\text{molecular volume (litres)}}{\text{molecular weight}}$$

As mentioned above, volume mixing ratios (ppb, etc.) are invariant with temperature and pressure, whilst μg m^{-3} concentrations change with temperature and pressure. The magnitude of this variation can be gauged from the variability of the molar volume (above). Generally, the molar volume is affected to the greatest degree by changes in temperature; a variation from 0°C to 27°C causes a change of 10% in molar volume, and thus μg m^{-3} concentrations. A rather extreme change in atmospheric pressure from 950 mb to 1020 mb gives a 7% change. Thus errors due to these factors can be significant, but are not massive.

At 25°C and 1013 mb pressure, the conversion factors are as follows:

	ppb to μg m^{-3} multiply by	μg m^{-3} to ppb multiply by
NO	1.23	0.81
NO_2	1.88	0.53
O_3	1.96	0.51
NH_3	0.69	1.44
HNO_3	2.60	0.38
H_2O_2	1.39	0.72

At 20°C and 1013 mb pressure, the conversion factors are as follows:

	ppb to μg m^{-3} multiply by	μg m^{-3} to ppb multiply by
NO	1.25	0.80
NO_2	1.91	0.52
O_3	2.00	0.50
NH_3	0.71	1.42
HNO_3	2.62	0.38
H_2O_2	1.41	0.71

APPENDIX 4: OZONE DATA AND THE ANNUAL MEAN MAP

Appendix 4:1 Ozone Data Statistics.

Table A4.1 [1/6] Annual Summary (S = summer period Apr-Sept, W = winter period Jan-Mar, Oct-Dec)

Site	Year	Mean	Median	Min	Max	S Mean	W Mean	%tile 84	%tile 90	%tile 95	%tile 98	%tile 99	%dc	S dc	W dc
AH	1986	25.0	25	1	110	25.7	23.3	30	32	37	51	69	37.9	52.1	23.7
AH	1987	24.5	26	0	76	28.6	19.0	34	36	40	50	57	68.8	77.9	59.7
AH	1988	30.3	31	0	106	33.2	27.8	38	43	49	56	61	87.7	83.1	92.3
AH	1989	30.9	32	0	109	35.4	26.9	41	44	48	58	68	93.0	86.9	99.1
AH	1990	33.0	33	0	124	36.7	29.1	40	45	57	72	84	96.0	98.3	93.6
AH	1991	28.2	29	0	87	33.5	23.0	40	43	48	56	61	97.6	97.1	98.2
AH	1992	30.2	31	0	101	33.8	26.6	39	42	49	65	71	98.6	98.0	99.2
AH	1993	29.9	32	1	96	33.0	27.1	38	41	45	54	63	91.8	86.3	97.4
AH	1994	32.4	33	0	93	35.7	29.0	42	45	48	56	61	97.8	98.0	97.7
AH	1995	31.8	32	0	100	35.9	27.7	40	44	55	74	83	96.9	96.8	97.0
AS	1979	21.9	19	0	137	22.0	19.3	34	41	50	63	75	31.0	58.7	3.1
AS	1980	23.3	22	0	105	23.6	13.7	37	42	50	57	62	49.3	95.4	3.2
AS	1981	22.8	18	0	118	23.2	17.6	38	44	59	73	86	33.8	62.5	4.9
AS	1982	26.5	24	0	123	26.5	0.0	40	46	56	67	74	29.9	59.6	0.0
AS	1983	23.7	21	0	153	24.1	15.2	38	44	60	78	90	38.2	72.7	3.5
AS	1984	29.5	26	0	113	29.5	0.0	47	54	68	84	91	32.8	65.6	0.0
BA	1976	58.7	52	0	203	58.7	0.0	100	122	150	183	200	5.7	11.5	0.0
BC	1992	17.8	17	0	69	20.0	14.4	28	32	36	41	47	80.6	98.1	63.1
BC	1993	16.3	16	1	54	18.0	14.6	27	30	33	36	39	97.3	97.0	97.2
BC	1994	17.9	18	0	57	20.4	15.3	29	32	35	39	42	94.8	95.3	93.8
BC	1995	19.3	19	0	78	22.5	16.1	31	34	37	43	50	95.7	95.9	95.0
BH	1992	15.1	14	0	86	18.5	10.9	26	30	34	40	48	63.0	70.4	55.6
BH	1993	14.3	12	0	77	17.0	11.6	26	30	33	37	41	97.2	96.5	97.2
BH	1994	16.7	16	0	82	19.4	14.1	29	32	36	41	46	95.5	93.9	96.6
BH	1995	16.6	15	0	94	19.7	13.5	28	32	36	44	58	97.1	96.3	97.2
BO	1993	15.5	14	0	89	17.3	13.6	27	31	35	39	42	96.3	96.9	95.1
BO	1994	18.7	19	0	74	20.9	16.5	30	33	37	41	45	96.4	94.9	97.3
BO	1995	19.3	19	0	93	22.3	16.1	32	35	39	47	58	95.9	96.9	94.4
BP	1990	9.6	5	0	108	13.0	6.3	18	23	29	39	54	49.1	48.2	49.5
BP	1991	9.6	6	0	63	12.6	6.8	19	23	28	35	42	80.7	78.8	82.0
BP	1992	10.8	8	0	76	13.4	7.8	20	24	30	37	46	86.4	93.1	79.7
BP	1993	11.1	8	0	98	14.6	7.6	21	25	30	37	44	97.0	95.6	97.9
BP	1994	12.4	9	0	102	16.3	8.6	23	28	34	45	55	93.6	92.3	94.2
BP	1995	10.4	7	0	56	13.2	9.2	20	23	27	31	34	67.9	38.7	96.7
BR	1981	7.0	5	0	44	0.0	7.0	14	17	20	24	28	21.3	0.0	42.7
BR	1982	19.6	18	0	110	26.3	13.3	34	39	47	59	70	95.4	92.3	98.0
BR	1983	19.9	19	0	112	23.8	15.7	32	35	42	53	60	93.4	95.5	90.7
BR	1984	19.5	18	0	113	24.9	14.2	33	38	46	55	68	97.8	97.8	97.7
BR	1985	20.1	19	0	114	23.4	13.7	32	36	43	50	65	70.1	90.7	48.8
BS	1994	17.9	17	0	97	21.5	14.2	30	33	37	47	55	97.0	96.6	97.0
BS	1995	17.7	16	0	96	21.7	13.6	30	34	39	56	70	96.6	96.5	96.1
BT	1981	18.9	17	0	79	22.1	12.4	32	36	41	48	57	74.6	99.0	49.5
BT	1982	22.4	21	0	111	28.3	16.6	37	41	49	65	75	97.0	95.4	98.1
BT	1983	21.6	21	0	99	25.7	17.4	34	38	47	56	65	97.8	97.9	97.1
BT	1984	20.8	19	0	111	26.2	15.5	35	40	51	62	70	97.3	95.9	98.8
BT	1985	20.4	20	0	109	25.2	15.5	33	37	43	52	61	99.3	99.1	98.9
BT	1986	23.0	23	0	103	25.9	20.2	37	40	45	53	61	99.3	98.8	99.3
BT	1987	18.1	17	0	104	20.5	14.6	32	36	42	50	59	82.6	95.7	68.9
BT	1988	16.5	16	0	68	19.0	10.9	27	31	36	42	45	70.7	98.3	43.0
BT	1989	16.5	16	0	83	19.9	12.8	27	31	37	47	61	92.5	94.4	90.0
BT	1990	18.8	18	0	138	20.2	17.0	29	32	39	53	67	86.8	97.2	75.8
BT	1991	12.2	10	0	49	0.0	12.2	24	28	32	36	39	41.8	0.0	83.7
BT	1992	14.8	14	0	95	18.5	11.0	26	29	34	43	52	98.6	99.9	97.2
BT	1993	14.8	14	0	97	16.3	13.5	25	28	32	38	45	88.4	84.2	92.0
BT	1994	20.2	21	0	82	23.6	17.0	31	34	38	43	48	94.4	90.0	98.3
BT	1995	19.3	18	0	106	22.7	15.0	30	34	40	54	63	88.8	97.7	79.3
BU	1986	25.3	26	1	73	25.9	24.6	33	35	38	41	45	87.4	94.9	79.3
BU	1987	22.6	23	0	96	26.2	19.0	33	36	40	46	52	97.1	97.8	95.7
BU	1988	27.2	28	0	89	29.5	25.0	35	38	42	49	53	97.1	95.1	99.0
BU	1989	27.0	28	0	103	28.5	25.5	38	40	44	50	57	97.6	98.7	95.9
BU	1990	27.3	28	0	100	27.4	27.3	37	39	43	52	59	96.7	97.4	95.5
BU	1991	23.7	25	1	81	26.6	20.6	33	35	38	42	46	97.2	98.4	95.5
BU	1992	27.2	28	0	85	29.3	25.1	37	39	44	50	57	98.7	99.3	98.0
BU	1993	25.8	27	1	60	26.8	24.8	35	37	40	44	46	96.3	98.5	93.5
BU	1994	27.8	29	0	71	30.2	25.4	38	40	43	46	50	98.3	97.4	98.6
BU	1995	26.4	28	0	79	28.5	24.8	36	38	40	45	49	80.9	71.5	89.7
CC	1992	13.8	10	0	98	17.4	8.5	25	30	40	55	68	61.3	72.6	50.0
CC	1993	14.9	12	1	85	18.5	11.1	26	30	35	43	52	95.0	96.5	92.9
CC	1994	16.6	15	0	107	19.5	13.6	28	31	36	43	50	96.4	97.1	95.2
CC	1995	17.9	16	0	103	21.9	13.7	29	33	39	58	74	96.3	97.0	95.1
CG	1979	19.0	17	0	128	19.0	0.0	33	40	48	63	71	32.1	63.5	0.0
CG	1982	24.9	22	2	119	24.9	0.0	39	47	57	70	79	20.0	39.4	0.0

Table A4.1 [2/6] Annual Summary (S = summer period Apr-Sept, W = winter period Jan-Mar, Oct-Dec)

Site	Year	Mean	Median	Min	Max	S Mean	W Mean	%tile 84	%tile 90	%tile 95	%tile 98	%tile 99	%dc	S dc	W dc
CG	1983	15.7	11	3	114	15.7	0.0	28	36	48	62	69	39.2	77.6	0.0
CG	1984	23.4	18	0	160	23.4	0.0	42	52	62	76	88	16.6	33.2	0.0
CG	1985	29.3	29	0	88	29.3	0.0	43	49	59	67	71	14.4	28.2	0.0
CH	1975	19.8	15	0	171	20.5	8.9	33	42	57	73	86	40.3	75.3	4.6
CH	1976	27.1	21	1	212	27.1	0.0	46	56	72	100	134	28.2	56.3	0.0
CH	1978	8.1	4	3	103	8.1	0.0	14	17	24	37	45	18.1	35.6	0.0
CH	1979	18.6	15	0	153	18.7	2.4	31	39	52	66	75	30.9	60.8	0.3
CH	1980	18.0	15	2	116	18.0	0.0	29	35	43	54	67	30.0	60.0	0.0
CH	1981	14.9	12	2	112	16.0	7.4	26	30	37	51	66	45.8	79.5	11.3
CH	1982	11.9	8	3	91	11.9	0.0	20	27	37	47	59	26.1	51.4	0.0
CH	1983	25.4	21	4	99	25.6	13.8	39	48	63	78	84	22.5	43.4	0.9
CH	1984	24.9	23	0	88	25.0	17.1	36	41	49	67	74	22.6	44.7	0.5
CH	1985	27.7	26	0	98	27.7	0.0	38	43	51	65	71	29.5	58.3	0.0
CH	1986	15.3	11	0	130	15.3	0.0	26	32	45	70	81	30.6	60.5	0.0
CH	1989	18.8	14	0	124	18.8	0.0	35	43	55	76	83	40.2	79.6	0.0
CK	1974	11.2	8	0	71	13.8	7.9	23	28	34	41	46	41.7	46.7	36.2
CL	1972	11.5	4	0	126	18.7	2.9	24	33	46	67	78	44.8	48.5	41.0
CL	1973	12.7	6	0	135	21.2	4.1	25	34	51	73	87	95.7	95.7	95.2
CL	1974	15.4	11	0	163	22.4	8.1	30	37	47	57	68	90.7	92.0	88.7
CL	1975	9.2	4	0	91	13.9	5.4	19	24	35	46	53	87.8	77.5	97.7
CL	1976	15.1	8	0	144	25.0	7.4	30	38	49	65	78	74.9	65.6	84.2
CL	1977	13.2	10	0	99	20.1	8.8	25	30	36	45	50	47.6	36.4	58.4
CL	1978	13.5	8	0	149	19.5	7.7	26	33	42	56	66	81.5	78.7	83.8
CL	1979	10.9	7	0	94	13.4	8.7	20	24	31	42	51	72.6	67.6	77.0
CL	1980	8.7	5	0	75	11.9	2.6	18	23	29	37	43	74.9	98.3	51.4
CL	1981	6.9	3	0	127	11.1	4.0	14	18	23	32	40	78.7	63.2	93.7
CL	1982	8.4	6	0	77	13.1	5.3	16	20	25	33	40	75.8	60.7	90.5
CL	1983	9.8	7	0	77	12.2	5.5	19	22	27	34	41	42.9	54.6	30.7
CL	1984	11.0	7	0	68	14.2	1.6	23	28	33	41	50	28.4	42.5	14.2
CL	1985	16.3	10	0	149	23.8	8.0	33	40	47	59	70	87.2	90.4	83.4
CL	1986	10.5	6	0	105	13.9	6.9	21	25	32	47	61	75.7	75.9	75.0
CL	1987	4.9	1	0	67	6.4	2.4	11	15	21	28	34	70.9	88.2	52.9
CL	1988	7.2	4	0	78	10.0	4.5	15	19	24	29	34	97.5	96.9	98.2
CL	1989	10.2	5	0	108	14.4	6.1	20	25	32	46	58	95.7	93.0	97.9
CL	1990	11.6	9	0	88	13.3	9.0	21	24	31	42	52	60.7	71.9	48.9
CR	1973	6.6	3	0	100	7.5	5.4	13	17	23	31	38	80.9	91.8	69.4
CR	1974	5.4	4	0	45	6.8	3.5	10	13	17	21	24	44.6	49.5	39.0
CT	1986	24.0	25	1	34	0.0	24.0	28	29	30	32	34	1.3	0.0	2.6
CT	1987	25.0	24	2	74	25.6	20.3	34	37	40	46	52	27.0	46.6	6.8
CT	1988	17.0	16	0	57	10.4	25.9	30	31	33	34	36	58.5	67.0	50.1
CT	1989	26.7	27	0	115	29.1	24.4	35	37	41	52	62	88.9	86.6	90.7
CT	1990	27.2	28	0	96	29.2	25.2	35	37	43	55	65	95.0	94.1	95.3
CV	1977	32.5	29	0	179	42.9	17.9	56	65	80	97	120	45.2	52.3	37.6
CV	1978	22.7	19	0	147	28.5	17.5	41	47	55	68	78	76.8	71.7	81.5
CV	1979	17.5	14	0	93	22.5	11.7	32	37	43	53	60	89.7	95.4	83.4
CV	1980	14.4	13	0	77	15.9	7.2	25	28	33	40	46	48.7	80.0	17.4
CW	1975	38.3	34	0	173	39.1	23.1	53	65	83	109	121	47.5	89.0	5.2
DE	1978	19.4	19	0	99	23.3	15.6	30	33	37	44	50	98.0	97.1	98.4
DE	1979	18.3	19	0	74	20.2	16.2	26	29	32	35	39	93.9	96.1	91.2
DE	1980	18.5	18	0	68	21.1	15.2	28	30	34	40	45	85.0	95.9	74.1
DH	1992	34.0	31	3	94	37.2	28.5	42	48	62	70	73	68.4	86.8	50.1
DH	1993	30.7	30	1	94	32.1	29.4	38	40	44	50	59	93.2	89.0	96.9
DH	1994	31.8	32	1	78	34.1	29.4	39	42	46	53	58	99.7	99.0	99.9
DR	1987	12.2	13	0	32	15.9	11.1	22	24	26	27	28	29.8	13.5	45.7
DR	1988	17.7	17	0	79	19.9	15.4	27	30	34	38	44	90.0	92.3	87.7
DR	1989	22.8	23	0	111	28.4	17.7	32	37	48	64	72	90.7	86.0	94.9
DR	1990	22.6	22	0	120	27.3	16.4	32	38	50	68	82	73.0	81.6	63.9
ED	1992	8.6	6	0	35	0.0	8.6	18	21	25	27	29	24.2	0.0	48.3
ED	1993	13.1	12	0	44	14.6	11.5	23	25	29	32	34	95.1	95.2	94.4
ED	1994	15.0	14	0	55	16.9	13.1	26	29	32	36	39	95.4	97.2	92.9
ED	1995	15.3	14	0	71	16.8	13.9	26	29	33	37	40	96.8	95.7	97.5
EK	1975	28.2	26	8	118	28.5	23.7	42	49	61	74	83	39.6	73.6	4.8
EM	1984	22.3	17	5	111	22.8	13.6	36	44	58	75	83	32.0	60.4	3.7
EM	1985	33.4	33	0	126	33.4	0.0	46	50	58	68	81	24.6	48.5	0.0
ES	1986	21.0	21	1	104	22.5	18.4	29	33	37	42	50	66.9	82.8	50.5
ES	1987	20.6	21	0	84	22.8	18.2	30	32	35	41	50	95.3	99.2	90.8
ES	1988	25.7	27	0	75	28.0	23.6	34	36	41	46	52	95.3	90.7	100.0
ES	1989	28.1	28	1	90	29.7	26.2	38	41	45	53	65	92.1	99.4	84.1
ES	1990	27.7	28	1	106	28.6	26.7	37	40	44	55	64	96.9	98.2	95.0
ES	1991	26.3	28	0	81	30.4	22.3	36	39	42	50	55	97.4	95.8	98.4
ES	1992	26.6	27	0	80	30.1	23.1	37	40	45	54	60	98.1	98.8	97.4
ES	1993	24.9	26	1	115	26.5	23.2	35	37	41	46	50	97.1	95.2	98.5
ES	1994	27.3	29	1	75	30.1	24.6	38	41	44	49	53	98.6	97.7	98.9
ES	1995	27.6	29	1	92	29.4	25.8	37	39	44	54	64	98.4	97.2	99.0
FL	1988	13.0	12	0	34	0.0	13.0	26	28	30	32	33	11.2	0.0	22.3
FL	1989	24.7	25	0	128	30.2	19.2	37	41	51	66	78	89.5	89.3	89.2
FL	1990	20.0	19	0	107	21.7	17.8	31	34	40	52	64	69.5	77.4	61.0

Table A4.1 [3/6] Annual Summary (S = summer period Apr-Sept, W = winter period Jan-Mar, Oct-Dec)

Site	Year	Mean	Median	Min	Max	S Mean	W Mean	%tile 84	%tile 90	%tile 95	%tile 98	%tile 99	%dc	S dc	W dc
GD	1986	22.1	21	1	93	25.5	18.1	28	34	39	68	84	45.3	48.6	41.5
GD	1987	28.5	27	0	92	32.7	23.5	37	40	48	64	77	76.5	83.2	69.2
GD	1988	30.4	30	0	82	34.2	25.8	38	43	50	58	66	87.4	95.4	79.5
GD	1989	30.7	30	0	109	34.2	27.3	38	42	50	65	73	93.7	93.1	93.8
GD	1990	31.8	31	0	114	34.5	28.7	38	43	53	66	75	89.4	95.2	83.1
GD	1991	29.1	29	0	94	34.4	22.8	38	41	49	61	68	92.3	98.9	85.1
GD	1992	30.9	30	1	141	37.6	24.2	41	46	57	67	77	98.4	99.0	97.9
GD	1993	31.4	31	1	119	33.1	29.6	38	41	46	54	68	98.4	97.6	98.7
GD	1994	32.4	32	1	87	35.9	28.8	40	43	47	53	61	97.8	96.9	98.1
GD	1995	31.7	31	0	94	35.1	28.4	38	42	51	67	74	98.7	98.6	98.2
GL	1983	19.2	19	0	104	23.8	13.8	32	36	42	52	69	47.9	51.5	43.7
GL	1984	15.1	14	0	82	19.0	11.3	26	30	36	47	53	94.1	93.4	94.9
GL	1985	8.1	7	0	108	10.9	4.5	15	17	20	25	32	79.6	88.5	70.1
GL	1986	11.8	10	0	57	14.4	7.8	23	26	30	34	37	64.7	76.9	51.9
GZ	1989	17.3	16	0	85	22.1	13.1	31	35	40	45	55	78.2	72.4	83.4
GZ	1990	18.6	18	0	96	21.7	15.6	31	34	38	51	61	81.4	78.1	84.2
GZ	1991	18.7	17	0	81	22.9	11.9	34	39	45	50	53	76.5	93.9	58.4
GZ	1992	17.9	16	0	113	21.4	13.9	32	36	42	52	63	91.9	97.7	86.2
GZ	1993	15.9	14	0	107	19.0	12.7	30	33	37	44	49	98.3	98.6	97.4
GZ	1994	18.4	18	0	71	22.2	14.5	33	36	40	45	50	96.5	97.3	95.1
GZ	1995	17.5	16	0	100	21.7	12.8	31	34	39	52	66	94.5	99.0	89.5
HM	1987	18.2	19	0	52	19.8	16.9	27	29	32	35	38	45.8	40.8	50.3
HM	1988	24.4	24	0	82	29.3	19.6	35	39	45	53	57	98.1	97.5	98.8
HM	1989	26.2	26	0	98	33.6	19.9	38	42	48	64	76	89.2	80.7	97.2
HM	1990	26.4	26	0	111	30.7	21.9	36	39	47	61	71	93.7	94.7	92.1
HM	1991	27.2	28	0	90	34.2	20.3	40	44	50	58	64	98.5	97.9	98.6
HM	1992	29.2	29	1	100	33.0	24.0	40	44	54	65	72	84.6	98.1	71.2
HM	1993	28.7	29	1	114	31.0	25.4	39	43	47	52	57	80.1	93.1	66.4
HM	1994	28.6	30	0	96	34.0	23.2	41	44	47	53	61	98.8	98.5	98.4
HM	1995	28.1	28	0	97	33.2	22.5	38	41	48	62	70	96.8	99.1	93.9
HN	1975	22.2	17	1	126	22.2	0.0	39	49	67	90	100	29.2	57.6	0.0
HN	1976	37.8	31	3	175	37.8	0.0	65	83	101	123	140	27.9	55.8	0.0
HO	1979	7.8	4	0	180	13.9	4.9	15	18	25	32	39	37.3	23.7	50.5
HO	1980	12.7	11	0	110	15.2	5.8	22	27	33	42	49	52.6	77.2	28.1
HR	1976	92.8	77	12	254	92.8	0.0	157	178	209	220	222	4.8	9.6	0.0
HR	1983	33.8	32	3	142	33.8	0.0	43	50	66	83	93	33.4	66.0	0.0
HR	1984	26.0	24	1	114	31.2	20.4	37	44	54	67	79	83.3	86.5	80.1
HR	1985	27.1	27	0	103	31.5	23.0	40	44	50	56	63	91.6	87.6	95.1
HR	1986	23.3	23	0	137	26.2	20.3	33	37	41	50	59	92.7	94.0	90.8
HR	1987	20.9	21	1	92	24.8	16.9	32	36	40	46	54	81.9	81.9	81.3
HR	1988	24.1	24	1	81	23.7	24.8	34	36	40	44	49	64.5	79.9	49.0
HR	1989	21.1	20	0	117	25.1	14.7	33	39	51	68	80	65.0	79.4	50.0
HR	1990	24.9	25	0	132	29.0	20.7	34	39	49	66	78	95.4	96.0	94.3
HR	1991	24.2	25	1	96	30.7	17.8	37	41	47	60	69	98.5	97.3	99.3
HR	1992	26.4	26	0	123	30.6	21.2	39	44	52	68	80	87.0	97.2	76.9
HR	1993	24.4	24	0	96	26.7	20.6	36	40	46	55	67	76.0	93.7	57.7
HR	1994	25.7	26	0	114	30.7	21.0	37	41	47	59	71	91.2	87.4	94.5
HR	1995	25.7	25	0	116	31.4	20.7	37	40	50	71	85	91.0	83.3	98.3
HU	1994	15.8	14	0	98	20.1	11.4	27	31	35	40	44	97.4	97.3	96.8
HU	1995	16.0	15	1	78	19.8	12.1	27	30	35	41	45	96.1	97.0	94.6
HZ	1981	23.8	23	0	99	26.6	20.0	34	39	45	57	69	58.4	67.2	49.0
HZ	1982	21.4	21	0	70	22.5	21.4	37	42	48	53	55	23.2	0.2	45.7
IS	1976	9.6	1	0	117	18.2	1.8	21	32	47	63	74	47.7	45.1	50.3
IS	1977	10.2	5	0	127	14.6	5.0	22	27	35	45	53	87.8	95.8	79.3
IS	1978	8.4	3	0	98	10.0	4.9	19	27	37	46	50	45.8	62.2	28.8
JH	1984	19.8	18	0	107	24.4	13.7	33	38	47	56	63	86.2	97.7	74.8
JH	1985	19.7	19	0	106	24.3	15.2	33	37	41	47	54	96.1	94.5	97.1
JH	1986	22.5	22	0	87	26.0	18.9	37	41	46	53	60	88.5	87.4	88.9
JH	1987	20.9	19	0	113	26.6	15.9	36	42	49	59	72	92.8	85.7	99.4
JH	1988	16.5	17	0	86	20.3	12.9	27	30	34	40	44	97.8	97.5	98.2
KW	1979	17.3	13	1	156	17.5	7.9	32	38	46	57	75	31.7	61.9	0.8
LB	1988	22.5	24	0	87	24.6	20.8	32	33	36	40	45	44.8	39.7	49.9
LB	1989	26.2	26	0	120	31.0	21.3	36	40	47	60	76	99.0	98.5	98.9
LB	1990	26.0	26	0	120	30.0	21.4	35	39	48	62	73	91.6	97.6	85.0
LB	1991	25.8	26	1	86	29.6	19.3	36	40	45	52	61	57.5	71.8	42.5
LB	1992	23.1	24	0	114	27.9	19.8	32	35	42	54	65	50.7	41.0	60.4
LB	1993	24.3	25	0	101	27.9	21.3	35	37	42	49	54	89.8	82.0	97.0
LB	1994	26.8	28	0	112	30.8	23.1	36	39	44	50	58	93.3	89.1	97.0
LB	1995	26.4	27	0	97	31.1	22.6	36	39	45	58	69	86.9	77.2	96.1
LC	1994	16.5	15	0	91	20.5	12.5	28	32	37	46	53	97.1	97.0	96.6
LC	1995	17.1	15	0	115	21.9	12.1	29	34	40	55	67	96.7	96.9	95.9
LD	1993	12.5	11	0	76	15.2	9.7	22	26	30	35	38	96.7	96.9	95.9
LD	1994	14.5	13	0	71	18.0	11.0	25	29	32	37	40	95.7	96.4	94.4
LD	1995	15.0	13	0	81	19.3	10.7	26	29	34	42	52	97.4	97.1	97.1
LH	1986	19.0	20	0	49	0.0	19.0	27	28	31	36	39	14.1	0.0	28.3
LH	1987	23.4	23	0	113	28.2	16.7	35	39	49	61	70	58.4	67.1	49.0
LH	1988	27.2	28	0	104	32.4	21.6	39	42	47	56	64	93.4	95.4	91.3

Table A4.1 [4/6] Annual Summary (S = summer period Apr-Sept, W = winter period Jan-Mar, Oct-Dec)

Site	Year	Mean	Median	Min	Max	S Mean	W Mean	%tile 84	%tile 90	%tile 95	%tile 98	%tile 99	%dc	S dc	W dc
LH	1989	30.6	31	0	136	36.9	23.8	44	50	60	76	87	95.7	98.1	92.7
LH	1990	32.0	31	0	161	37.4	26.1	43	50	61	77	87	89.8	92.8	86.2
LH	1991	24.9	24	0	124	31.5	18.4	37	41	48	59	67	98.5	97.4	98.9
LH	1992	28.9	29	0	104	36.3	21.9	42	47	56	70	80	89.6	87.8	91.5
LH	1993	27.8	28	1	117	32.3	21.3	39	45	52	63	72	79.1	92.3	65.2
LH	1994	30.6	31	0	117	34.9	25.4	42	46	53	65	73	88.4	96.0	80.3
LH	1995	30.1	29	0	134	36.2	24.0	41	46	57	80	93	95.3	94.3	95.8
LN	1986	16.8	16	0	61	18.1	16.4	30	34	38	44	48	30.1	13.1	46.6
LN	1987	16.6	15	0	80	20.9	12.9	30	35	40	47	53	92.5	86.9	97.5
LN	1988	16.1	16	0	95	20.0	12.1	26	29	33	40	45	97.6	99.5	95.7
LR	1987	22.3	24	0	88	24.4	18.7	33	35	39	46	52	66.2	82.0	49.7
LR	1988	24.8	26	0	74	26.5	22.8	34	38	42	48	54	89.7	97.5	81.8
LR	1989	25.0	27	0	107	26.6	23.5	36	38	42	48	57	99.2	98.5	99.3
LR	1990	25.7	28	0	94	25.8	25.6	36	38	42	50	58	96.2	94.4	97.5
LR	1991	23.1	25	0	94	25.9	20.3	33	35	39	46	53	99.0	98.4	99.1
LR	1992	25.6	27	0	86	27.9	23.8	36	38	42	51	59	86.9	78.0	95.8
LR	1993	24.2	27	1	62	23.9	24.4	35	37	39	43	45	98.4	98.5	97.7
LR	1994	25.5	27	0	70	25.9	25.1	37	40	43	46	48	98.8	98.5	98.6
LR	1995	24.5	26	0	88	25.5	23.3	35	38	42	50	58	93.1	97.4	88.3
LV	1993	13.5	12	0	50	16.6	9.7	25	27	31	34	37	56.1	61.5	50.2
LV	1994	17.5	17	1	61	20.2	14.7	30	33	36	39	42	96.7	95.6	97.2
LV	1995	18.8	18	1	81	23.2	14.3	33	36	40	47	56	94.3	95.4	92.8
LY	1992	9.5	6	0	73	12.8	5.9	19	23	29	38	48	91.9	96.7	87.1
LY	1993	9.1	6	0	93	11.5	6.7	18	21	27	32	38	96.4	95.2	97.1
LY	1994	10.7	7	0	95	13.7	7.8	20	24	29	35	43	95.9	95.4	95.8
LY	1995	10.5	7	0	102	13.3	7.6	19	23	29	36	48	92.7	94.0	90.8
MD	1995	17.5	17	0	96	21.7	13.4	28	31	36	47	59	49.1	47.7	49.9
MH	1987	26.3	27	1	64	26.9	25.3	32	33	35	41	45	72.2	95.6	48.1
MH	1988	33.3	33	5	65	34.2	32.4	40	42	44	47	51	93.3	97.8	88.9
MH	1989	33.8	35	0	99	34.5	33.1	42	43	47	53	59	90.8	86.1	95.1
MH	1990	34.6	35	2	83	35.3	34.0	41	43	48	55	60	96.7	95.3	97.6
MH	1991	34.8	34	0	87	36.9	32.6	43	46	51	60	64	96.2	96.6	95.2
MH	1992	33.1	33	0	83	33.7	32.6	40	42	45	50	57	98.9	98.6	99.1
MH	1993	34.3	35	1	66	33.8	34.8	43	45	47	49	51	91.0	97.6	83.7
MH	1994	35.7	36	6	62	35.6	35.7	44	46	48	50	52	97.8	97.0	98.1
MH	1995	34.7	35	2	80	36.3	33.0	43	45	49	57	64	94.6	97.6	91.0
MP	1995	---	---	---	---	---	---	---	---	---	---	---	0.0	0.0	0.0
NC	1992	14.7	14	0	53	16.8	11.4	25	28	32	38	41	79.4	95.8	62.9
NC	1993	15.0	14	0	57	14.8	15.5	25	29	32	36	38	68.8	90.1	46.8
NC	1994	---	---	---	---	---	---	---	---	---	---	---	0.0	0.0	0.0
NC	1995	---	---	---	---	---	---	---	---	---	---	---	0.0	0.0	0.0
NN	1989	26.0	26	0	102	31.8	19.6	39	44	50	60	71	79.3	82.6	75.5
NN	1990	29.4	28	0	139	32.8	23.9	40	46	54	68	81	57.4	70.4	43.8
NW	1983	18.6	14	2	107	18.6	0.0	31	39	54	68	77	38.5	76.3	0.0
SB	1973	30.6	28	0	142	31.3	23.7	46	58	69	87	100	22.6	40.1	4.4
SB	1974	31.3	32	0	85	31.3	0.0	43	47	51	59	63	14.8	29.0	0.0
SB	1975	38.4	36	1	161	38.4	0.0	56	61	73	94	109	31.5	62.4	0.0
SB	1976	24.0	21	0	104	36.4	15.9	41	49	64	78	83	27.3	21.6	33.0
SB	1977	28.8	27	0	113	36.0	22.3	45	51	61	75	88	63.1	59.2	66.4
SB	1978	32.7	31	0	127	35.1	26.9	49	54	61	74	86	49.5	69.4	28.9
SB	1979	20.8	19	0	83	24.9	11.2	33	38	45	56	64	42.0	58.2	25.2
SB	1980	16.4	16	0	63	18.7	11.5	25	29	34	39	44	58.3	80.1	36.5
SB	1981	24.4	19	0	207	29.6	15.4	38	47	61	92	110	78.1	97.9	57.7
SB	1982	25.3	24	0	124	29.6	20.3	38	42	49	60	71	90.4	96.0	84.2
SB	1983	27.5	26	0	133	33.8	14.4	42	46	55	69	79	66.0	88.5	42.9
SB	1984	22.5	20	0	124	27.2	16.3	35	40	47	56	61	79.8	90.5	69.1
SB	1985	17.7	17	0	88	24.0	13.2	31	35	41	50	59	69.6	57.8	81.0
SB	1987	21.6	21	0	100	25.4	14.7	34	38	43	51	59	58.6	74.4	42.1
SB	1988	24.1	24	0	106	30.5	17.3	38	42	47	54	60	92.6	95.2	90.1
SB	1989	24.9	24	0	122	34.1	17.0	39	44	52	65	76	91.5	83.4	99.2
SB	1990	25.4	25	0	145	30.9	19.8	37	40	49	63	74	96.9	97.2	96.0
SB	1991	27.4	27	0	90	32.3	19.3	42	46	51	58	64	65.8	81.7	49.2
SB	1992	25.8	25	0	123	32.6	19.0	38	43	53	67	74	94.4	95.1	93.7
SB	1993	26.6	27	0	122	31.9	21.3	39	44	51	58	64	99.0	98.5	99.1
SB	1994	26.0	25	0	127	32.9	18.6	40	44	50	61	74	95.6	97.7	92.9
SB	1995	25.6	26	0	112	30.9	20.2	37	41	47	61	71	97.4	98.2	96.2
SD	1982	29.6	29	0	133	32.2	24.5	46	51	59	74	83	73.3	95.6	50.3
SD	1983	29.8	31	0	156	33.8	25.8	46	50	56	69	80	98.1	97.5	98.1
SD	1984	28.4	29	0	120	33.6	21.1	45	49	57	66	79	56.4	66.1	46.6
SH	1994	17.7	17	0	91	21.4	14.0	30	33	37	45	52	96.9	95.9	97.3
SH	1995	15.5	14	0	93	19.3	13.6	28	31	35	39	43	72.9	47.8	97.6
SO	1985	25.7	24	0	144	27.3	19.2	40	46	55	65	76	41.0	65.4	15.9
SO	1986	32.1	31	0	128	35.3	16.9	47	52	62	76	87	38.1	62.2	13.3
SO	1987	29.9	24	0	159	29.9	0.0	55	62	76	93	105	17.5	34.4	0.0
ST	1976	65.9	61	2	207	65.9	0.0	113	127	139	157	180	5.6	11.3	0.0
ST	1977	23.1	22	0	135	25.8	16.2	38	42	48	58	66	65.9	93.5	37.7
ST	1978	16.1	13	0	100	20.0	12.2	29	34	41	51	60	94.4	93.3	95.0

Table A4.1 [5/6] Annual Summary (S = summer period Apr-Sept, W = winter period Jan-Mar, Oct-Dec)

Site	Year	Mean	Median	Min	Max	S Mean	W Mean	%tile 84	%tile 90	%tile 95	%tile 98	%tile 99	%dc	S dc	W dc
ST	1979	14.1	12	0	108	17.9	9.8	25	28	34	45	57	86.3	91.0	81.1
ST	1980	9.7	8	0	84	11.3	8.0	17	20	25	33	39	90.6	95.1	86.2
ST	1981	7.0	5	0	68	8.0	6.1	13	15	18	23	28	91.2	87.4	94.4
ST	1982	17.3	13	0	164	24.4	11.3	30	36	49	74	95	81.5	73.8	88.8
ST	1983	20.0	19	0	168	23.7	14.6	32	37	48	66	75	76.3	90.3	61.6
ST	1984	20.0	16	0	174	27.3	12.3	36	45	56	69	88	95.7	98.0	93.3
ST	1985	14.5	12	0	123	18.5	10.0	26	31	38	50	60	88.7	93.1	83.7
ST	1986	13.4	7	0	103	15.7	10.7	25	31	46	58	68	60.5	65.0	55.4
ST	1987	10.4	7	0	85	13.7	6.5	21	25	31	42	53	79.6	85.5	73.1
ST	1988	12.1	10	0	70	14.8	9.1	23	27	32	41	47	92.0	96.2	87.9
ST	1989	12.6	9	0	101	16.1	9.0	24	28	35	48	62	90.4	90.3	90.0
ST	1990	15.3	12	0	136	18.5	12.3	26	31	39	54	72	91.3	88.0	94.0
ST	1991	13.1	10	0	84	17.4	9.5	24	28	34	42	52	89.6	80.4	98.4
ST	1992	14.2	11	0	89	17.5	9.4	24	29	38	55	65	80.2	93.9	66.5
ST	1993	15.3	13	0	133	18.6	12.0	26	30	36	45	56	98.2	97.2	98.6
ST	1994	17.3	17	0	47	22.3	15.7	29	31	34	37	39	31.7	14.9	48.0
SV	1987	30.6	31	0	92	32.2	27.5	38	41	45	50	56	71.4	92.4	49.8
SV	1988	33.9	34	1	73	34.2	33.5	41	43	47	52	57	96.6	96.4	96.7
SV	1989	32.3	33	6	80	32.3	32.2	40	42	44	48	51	78.9	66.9	90.4
SV	1990	33.0	33	9	80	33.6	32.2	40	42	46	53	58	88.3	96.1	79.8
SV	1991	32.5	32	4	74	36.7	27.9	42	46	50	56	61	88.6	92.3	84.4
SV	1992	34.5	34	6	77	35.1	33.9	43	45	49	59	63	94.9	95.4	94.5
SV	1993	34.1	34	4	66	34.2	34.1	42	44	47	50	52	80.8	80.6	80.3
SV	1994	36.4	37	6	72	36.6	36.0	45	47	50	54	60	73.5	84.0	62.4
SV	1995	33.7	34	5	86	33.7	33.7	41	43	46	51	59	94.9	96.3	93.0
SW	1994	18.5	17	1	40	0.0	18.5	33	35	36	38	39	8.4	0.0	16.9
SW	1995	20.4	18	0	114	23.0	18.0	34	38	43	56	71	96.3	94.7	97.4
SY	1986	21.9	20	0	97	23.5	18.4	33	37	43	50	57	67.1	90.1	43.5
SY	1987	21.7	22	0	133	27.2	16.0	34	37	43	59	71	96.6	97.2	95.4
SY	1988	17.2	18	0	68	19.2	15.3	25	28	32	37	40	95.7	93.9	97.5
TD	1975	22.1	18	0	140	22.1	15.6	40	50	68	91	102	40.9	80.8	0.2
TD	1976	40.7	35	1	211	41.5	28.7	63	78	101	130	153	41.0	76.6	5.4
TD	1978	25.2	21	3	157	25.4	19.7	40	49	63	91	102	36.7	70.2	2.4
TD	1982	20.4	17	3	123	20.4	0.0	34	40	54	69	80	28.2	55.7	0.0
TD	1983	33.8	32	8	137	33.8	0.0	50	56	69	85	95	28.5	56.2	0.0
TD	1984	22.4	19	0	117	23.9	11.7	38	44	56	72	78	40.2	70.7	9.8
TD	1985	24.1	23	0	104	24.1	0.0	37	44	51	66	75	29.6	58.5	0.0
TD	1987	14.3	11	0	118	17.8	11.2	27	32	38	48	61	46.2	42.0	49.9
TD	1988	20.8	17	0	123	24.3	18.6	39	47	57	71	78	66.9	51.3	82.5
TD	1989	20.0	18	0	117	23.4	14.7	34	40	50	66	79	75.6	91.8	58.8
TD	1990	17.7	16	0	142	22.4	14.1	30	34	44	60	78	81.9	70.9	92.4
TD	1991	14.5	12	0	92	19.6	9.6	28	31	37	47	55	94.9	92.0	97.3
TH	1981	17.6	15	0	98	21.8	8.9	31	38	46	52	60	74.3	99.4	48.5
TH	1982	19.4	17	0	110	26.5	12.5	34	39	47	63	77	98.7	97.0	99.8
TH	1983	20.7	20	0	100	25.5	16.0	33	37	45	53	62	97.2	95.8	98.1
TH	1984	20.0	18	0	110	25.4	14.6	34	39	47	57	64	98.0	97.4	98.6
TH	1985	19.7	19	0	99	24.4	14.9	33	36	42	51	58	94.9	96.1	93.2
TH	1986	21.3	21	0	90	24.1	18.4	35	38	42	48	56	99.6	99.4	99.4
TH	1987	19.1	18	0	96	24.4	13.8	34	39	44	52	66	94.1	93.1	94.7
TH	1988	15.3	14	0	116	19.3	11.8	27	31	36	44	48	91.1	84.4	97.8
WB	1981	8.3	7	0	32	0.0	8.3	15	17	19	21	23	25.0	0.0	50.2
WB	1982	18.3	16	0	109	24.5	12.0	31	36	42	56	65	99.5	99.2	99.2
WB	1983	19.6	19	0	93	23.7	15.5	32	36	42	51	56	98.3	98.4	97.7
WB	1984	16.2	17	1	39	0.0	16.2	27	29	31	33	37	10.7	0.0	21.4
WC	1985	43.6	41	10	98	43.6	0.0	63	67	72	79	84	4.0	7.5	0.0
WC	1986	15.4	15	0	99	19.6	13.4	21	22	25	32	54	32.8	20.6	44.6
WC	1987	19.2	20	0	89	25.9	14.1	29	32	37	41	48	77.6	66.6	88.0
WC	1988	24.7	24	0	75	27.6	21.6	33	37	43	50	55	95.8	98.4	93.2
WC	1989	25.9	26	0	107	29.6	22.9	35	38	44	57	68	86.3	77.5	94.7
WC	1990	26.7	27	0	102	28.7	24.7	35	37	44	57	65	94.6	95.5	93.2
WC	1991	30.7	31	1	95	36.4	24.8	41	46	51	61	66	97.1	98.8	94.8
WC	1992	28.4	29	0	107	31.4	25.5	36	38	45	56	62	98.9	99.3	98.4
WC	1993	27.5	28	0	115	30.2	24.5	36	39	44	53	62	95.1	98.1	91.7
WC	1994	29.2	30	1	87	32.8	25.7	39	42	46	52	57	97.4	96.2	98.0
WC	1995	31.6	31	0	104	34.1	28.5	40	44	53	69	76	89.3	98.2	79.9
WR	1985	27.7	28	0	88	31.0	24.2	38	41	45	50	55	94.0	95.6	91.9
WR	1986	26.6	28	1	75	27.4	25.6	36	38	41	44	48	88.5	92.2	84.3
WR	1987	24.7	26	0	98	28.1	21.4	35	38	41	47	54	87.9	85.7	89.6
WR	1988	25.4	28	2	44	0.0	25.4	33	35	36	38	39	15.8	0.0	31.6
WV	1995	3.4	2	0	14	0.0	3.4	7	9	10	12	13	3.6	0.0	7.1
YK	1986	13.7	13	1	36	0.0	13.7	23	24	26	28	29	10.4	0.0	20.9
YK	1987	14.8	14	0	76	23.1	11.2	27	29	33	38	42	60.2	35.5	84.5
YK	1988	11.9	11	0	49	15.4	8.4	19	23	28	33	37	95.0	95.0	95.0
YK	1989	9.5	9	0	59	13.8	6.8	16	18	21	29	36	70.3	53.0	87.2
YK	1990	10.8	10	0	64	13.2	8.3	17	19	22	27	34	93.4	94.5	91.8
YW	1987	21.4	22	0	94	21.3	21.5	30	31	34	42	54	42.7	46.8	38.0
YW	1988	28.7	30	0	109	30.2	27.3	38	40	43	49	55	94.7	92.6	96.8

Table A4.1 [6/6] Annual Summary (S = summer period Apr-Sept, W = winter period Jan-Mar, Oct-Dec)

Site	Year	Mean	Median	Min	Max	S Mean	W Mean	%tile 84	%tile 90	%tile 95	%tile 98	%tile 99	%dc	S dc	W dc
YW	1989	31.6	31	1	130	36.3	27.2	43	47	58	76	88	96.4	93.4	98.9
YW	1990	33.3	33	1	147	37.4	29.1	42	47	60	74	86	91.3	90.8	91.2
YW	1991	30.1	31	0	126	35.7	24.4	42	47	52	64	73	98.4	98.1	98.2
YW	1992	29.3	29	0	115	33.9	25.0	40	45	52	67	77	97.2	95.5	98.9
YW	1993	27.5	29	1	99	30.5	24.6	38	42	46	55	64	84.2	82.4	85.3
YW	1994	29.4	30	0	108	31.3	27.7	39	43	47	52	60	97.6	95.5	99.1
YW	1995	30.7	31	0	130	35.0	26.4	40	44	56	76	87	98.6	98.2	98.5

See Table A4.3 for an index of site references.

Table A4.2 [1/6] AOT40 values for forests and crops (forests Apr-Sept daylight hours, crops May-Jul daylight hours)

Site	Year	Forest	% dc Forest period	Wheat/Crops	%dc Wheat period
AH	1986	33333	50.9	3333	33.3
AH	1986	1453	50.9	1340	38.0
AH	1987	1905	78.4	608	81.2
AH	1988	5787	82.4	3669	73.1
AH	1989	7320	86.1	5689	76.4
AH	1990	12697	97.7	8964	97.0
AH	1991	5748	96.7	2244	95.9
AH	1992	8142	98.3	6692	97.6
AH	1993	4318	84.2	2892	78.5
AH	1994	7479	97.7	5712	97.9
AH	1995	11186	96.6	5313	95.8
AS	1979	3854	61.0	2295	72.1
AS	1980	4852	94.9	2718	92.5
AS	1981	6527	62.3	1437	65.5
AS	1982	5417	61.4	3647	59.4
AS	1983	8222	73.2	6677	83.9
AS	1984	10399	68.6	6938	84.2
BA	1976	11022	12.8	11022	23.6
BC	1992	513	97.5	512	96.4
BC	1993	65	96.8	55	95.6
BC	1994	407	95.0	397	98.2
BC	1995	1291	95.4	635	95.9
BH	1992	1167	66.9	931	44.7
BH	1993	698	96.0	534	94.3
BH	1994	1251	93.2	1218	92.3
BH	1995	3508	95.8	2212	96.3
BO	1993	827	96.7	786	94.9
BO	1994	1239	94.3	1179	93.0
BO	1995	3693	96.7	2107	95.2
BP	1990	1769	47.0	672	31.0
BP	1991	593	99.1	256	98.6
BP	1992	1053	92.7	810	87.8
BP	1993	1229	96.3	978	97.9
BP	1994	3100	93.6	2932	99.5
BP	1995	43	38.6	41	44.3
BR	1981	---	0.0	---	0.0
BR	1982	8658	91.8	6131	91.4
BR	1983	5600	95.6	4168	97.2
BR	1984	8592	97.4	4099	99.4
BR	1985	4484	90.6	1889	83.5
BS	1994	3414	96.4	3344	98.7
BS	1995	6535	96.9	3785	98.4
BT	1981	2931	99.4	739	99.5
BT	1982	10570	95.3	6837	92.2
BT	1983	7723	98.6	5070	99.0
BT	1984	10381	96.5	5120	99.9
BT	1985	5434	99.4	3765	99.4
BT	1986	5887	99.4	4509	99.8
BT	1987	3638	96.1	2175	99.6
BT	1988	923	97.9	428	96.7
BT	1989	3525	95.7	3213	99.6
BT	1990	5406	97.6	3171	99.5
BT	1991	---	0.0	---	0.0
BT	1992	2438	99.9	2073	99.9
BT	1993	1448	83.7	1421	74.0
BT	1994	1982	90.5	1718	91.5
BT	1995	4989	98.2	2156	99.2
BU	1986	843	95.2	763	94.1
BU	1987	2548	98.3	628	98.5
BU	1988	3366	94.9	2990	94.3
BU	1989	4578	99.4	3964	99.3
BU	1990	3866	98.2	2424	98.5
BU	1991	1191	98.5	429	98.3
BU	1992	3736	99.1	3115	98.5
BU	1993	892	98.9	584	99.6

Table A4.2 [2/6] AOT40 values for forests and crops (forests Apr-Sept daylight hours, crops May-Jul daylight hours)

Site	Year	Forest	% dc Forest period	Wheat/Crops	%dc Wheat period
BU	1994	2373	97.2	1739	95.2
BU	1995	1605	72.0	1276	81.1
CC	1992	3883	73.0	3857	83.4
CC	1993	1949	96.4	1726	96.3
CC	1994	2278	97.0	2203	99.0
CC	1995	6689	97.0	3675	98.6
CG	1979	3678	66.9	3089	87.1
CG	1982	3667	40.3	1621	28.8
CG	1983	3971	79.6	3040	93.0
CG	1984	4588	35.0	3193	37.2
CG	1985	2773	29.4	2341	32.2
CH	1975	7039	78.4	4987	96.1
CH	1976	10655	60.1	6262	72.3
CH	1978	343	36.5	209	25.1
CH	1979	3405	65.7	2802	76.4
CH	1980	2023	60.3	851	56.0
CH	1981	2647	79.3	53	70.7
CH	1982	1034	52.7	352	48.1
CH	1983	4980	42.7	4335	37.9
CH	1984	2674	50.2	2625	70.8
CH	1985	3630	58.5	2115	60.0
CH	1986	3404	67.5	3144	73.1
CH	1989	6672	80.8	5161	93.0
CK	1974	425	45.9	0	31.9
CL	1972	4878	47.1	2217	33.4
CL	1973	12590	95.4	6165	92.6
CL	1974	7690	92.1	5508	93.7
CL	1975	2240	76.3	893	66.2
CL	1976	8049	64.9	4041	54.4
CL	1977	1141	37.4	1115	41.5
CL	1978	4972	78.5	4578	92.3
CL	1979	1579	65.8	609	48.5
CL	1980	807	97.0	191	97.2
CL	1981	1627	64.0	57	71.9
CL	1982	679	57.8	101	26.2
CL	1983	359	57.1	315	72.5
CL	1984	572	43.1	278	51.6
CL	1985	6671	90.7	3458	92.0
CL	1986	2703	80.3	2454	99.1
CL	1987	570	88.7	346	88.4
CL	1988	332	96.9	108	96.0
CL	1989	3493	93.4	2933	89.0
CL	1990	1774	74.9	1222	90.5
CR	1973	836	90.9	793	88.5
CR	1974	5	51.4	5	71.3
CT	1986	---	0.0	---	0.0
CT	1987	720	51.1	719	68.3
CT	1988	93	71.8	93	81.1
CT	1989	4837	90.5	4582	88.0
CT	1990	5924	99.1	4151	99.6
CV	1977	21468	54.7	18293	76.6
CV	1978	10164	73.3	8500	85.9
CV	1979	5198	96.0	2789	92.7
CV	1980	646	79.7	356	80.2
CW	1975	23806	90.8	12279	98.7
DE	1978	2156	97.3	2094	98.4
DE	1979	294	95.4	252	95.9
DE	1980	803	95.5	662	93.0
DH	1992	9838	87.7	9504	97.1
DH	1993	3336	89.4	1811	82.2
DH	1994	4259	99.7	3997	100.0
DR	1987	0	13.0	---	0.0
DR	1988	901	95.6	498	95.8
DR	1989	8502	89.2	7643	86.5
DR	1990	8232	86.3	5753	96.6
ED	1992	---	0.0	---	0.0
ED	1993	6	95.5	6	99.1
ED	1994	100	97.4	100	99.1
ED	1995	448	95.4	154	96.4
EK	1975	7350	75.1	5532	82.4
EM	1984	5949	60.8	3760	61.2
EM	1985	5839	49.1	3271	43.0
ES	1986	1680	84.3	1486	92.0
ES	1987	2143	99.5	476	100.0
ES	1988	2604	91.8	2236	98.3
ES	1989	6514	99.9	5398	100.0
ES	1990	5661	98.5	3885	98.6

Table A4.2 [3/6] AOT40 values for forests and crops (forests Apr-Sept daylight hours, crops May-Jul daylight hours)

Site	Year	Forest	% dc Forest period	Wheat/Crops	%dc Wheat period
ES	1991	3412	95.3	1594	94.6
ES	1992	5681	98.3	4909	96.9
ES	1993	3025	95.9	2090	99.1
ES	1994	3952	97.8	3259	97.5
ES	1995	5758	97.3	3355	98.1
FL	1988	---	0.0	---	0.0
FL	1989	11249	93.9	9128	94.6
FL	1990	3975	82.2	2589	96.8
GD	1986	2904	49.1	2904	63.8
GD	1987	5660	84.0	2914	89.8
GD	1988	6241	95.2	5011	97.9
GD	1989	8530	93.4	7722	89.0
GD	1990	8037	96.0	5418	97.5
GD	1991	5727	99.3	2987	98.8
GD	1992	11456	98.5	9633	97.7
GD	1993	5175	97.7	3081	96.5
GD	1994	5505	97.2	4563	96.5
GD	1995	8793	99.2	4719	99.8
GL	1983	2966	52.4	2332	49.0
GL	1984	2460	93.7	1351	94.8
GL	1985	619	88.2	619	85.2
GL	1986	122	77.0	77	76.4
GZ	1989	2529	74.5	2390	84.6
GZ	1990	3850	82.5	2821	83.7
GZ	1991	3745	93.4	2008	89.6
GZ	1992	5305	98.6	4799	97.6
GZ	1993	2337	99.2	1566	98.7
GZ	1994	2312	97.3	1983	97.9
GZ	1995	4927	99.3	2272	99.9
HM	1987	89	38.4	36	16.1
HM	1988	4723	97.8	3343	99.2
HM	1989	8020	81.0	6728	72.7
HM	1990	6637	95.5	4534	95.4
HM	1991	7986	98.7	4139	98.3
HM	1992	8864	97.9	7537	96.9
HM	1993	4790	93.4	3604	95.6
HM	1994	6778	98.9	5622	98.2
HM	1995	7719	99.4	4594	99.3
HN	1975	7686	62.3	3925	98.4
HN	1976	23979	58.1	17869	71.1
HO	1979	235	21.4	---	0.0
HO	1980	856	80.3	421	93.8
HR	1976	16541	10.8	16541	19.9
HR	1983	8326	69.1	8015	100.0
HR	1984	10359	87.0	6089	96.8
HR	1985	6655	88.1	3536	83.4
HR	1986	4133	93.8	3755	92.1
HR	1987	2763	83.1	1265	94.1
HR	1988	1409	80.0	613	84.5
HR	1989	8353	79.6	6602	93.9
HR	1990	10509	95.6	6850	94.7
HR	1991	9081	97.6	3604	97.3
HR	1992	11605	97.3	9503	97.7
HR	1993	5717	94.2	4446	92.6
HR	1994	8726	87.3	7296	78.1
HR	1995	10993	85.1	6487	98.3
HU	1994	899	97.0	879	95.6
HU	1995	1319	96.9	1085	95.4
HZ	1981	3476	68.0	1222	71.3
HZ	1982	0	0.6	---	0.0
IS	1976	4827	42.7	1319	23.0
IS	1977	2663	96.0	2285	98.6
IS	1978	1080	65.8	860	99.8
JH	1984	6816	97.7	3358	96.3
JH	1985	3211	95.2	2173	95.1
JH	1986	5512	87.9	3229	92.7
JH	1987	9009	86.5	5507	97.0
JH	1988	974	97.3	421	95.4
KW	1979	3343	62.0	2230	61.0
LB	1988	618	37.5	22	17.5
LB	1989	9310	99.4	8419	99.9
LB	1990	7910	98.4	5628	99.8
LB	1991	2903	74.9	2274	89.0
LB	1992	2980	39.5	2898	30.6
LB	1993	3253	82.7	2230	87.0
LB	1994	4425	90.6	3935	96.0
LB	1995	5704	78.5	4339	95.7

Table A4.2 [4/6] AOT40 values for forests and crops (forests Apr-Sept daylight hours, crops May-Jul daylight hours)

Site	Year	Forest	% dc Forest period	Wheat/Crops	%dc Wheat period
LC	1994	3021	96.7	2943	95.2
LC	1995	5599	96.7	3299	95.2
LD	1993	267	96.9	261	95.6
LD	1994	557	96.1	548	98.3
LD	1995	2140	97.1	1131	98.9
LH	1986	---	0.0	---	0.0
LH	1987	4426	68.0	3084	73.0
LH	1988	6460	95.3	3595	96.5
LH	1989	16803	98.6	12913	98.8
LH	1990	16362	94.1	8590	95.9
LH	1991	7441	98.2	3227	98.5
LH	1992	11787	87.0	9613	84.1
LH	1993	8438	93.4	6326	95.5
LH	1994	10499	97.1	7899	95.5
LH	1995	14637	93.2	9738	95.2
LN	1986	321	11.1	---	0.0
LN	1987	2313	86.7	805	85.1
LN	1988	1233	99.4	488	99.8
LR	1987	1981	85.2	703	89.2
LR	1988	3145	97.8	2454	99.3
LR	1989	4615	99.3	4019	99.9
LR	1990	3889	94.0	3272	93.4
LR	1991	2902	99.2	1110	98.8
LR	1992	3893	80.9	3655	98.5
LR	1993	1214	98.8	779	98.6
LR	1994	2063	98.7	1356	99.9
LR	1995	3718	97.5	1963	99.0
LV	1993	76	62.4	34	67.6
LV	1994	345	95.1	301	92.1
LV	1995	2480	95.0	1201	92.5
LY	1992	1449	95.8	1217	94.5
LY	1993	833	94.9	702	93.2
LY	1994	1353	94.6	1299	91.8
LY	1995	2111	93.1	1831	90.6
MD	1995	1814	46.0	643	29.9
MH	1987	574	96.3	85	95.8
MH	1988	2287	97.2	1866	97.0
MH	1989	4616	87.3	4002	97.3
MH	1990	5398	94.4	3824	96.3
MH	1991	5884	96.6	2412	96.0
MH	1992	3783	98.4	3059	97.6
MH	1993	3535	97.4	1964	95.7
MH	1994	3980	97.9	2182	97.6
MH	1995	6715	98.1	3035	99.5
MP	1995	---	0.0	---	0.0
NC	1992	140	95.0	129	92.8
NC	1993	54	90.9	54	91.5
NC	1994	---	0.0	---	0.0
NC	1995	---	0.0	---	0.0
NN	1989	7965	83.3	4817	81.8
NN	1990	7861	72.7	4119	79.0
NW	1983	5268	78.1	4230	89.0
SB	1973	6655	40.0	1474	27.1
SB	1974	1546	31.3	729	28.3
SB	1975	12663	63.0	8341	72.5
SB	1976	4933	20.1	234	3.5
SB	1977	9179	59.9	5624	62.7
SB	1978	11096	71.3	8519	76.4
SB	1979	2444	59.3	1775	69.0
SB	1980	397	81.1	266	93.3
SB	1981	15426	98.8	1453	99.9
SB	1982	8101	96.8	4448	99.0
SB	1983	9191	90.9	6349	100.0
SB	1984	4644	91.8	1430	97.0
SB	1985	2524	55.4	908	36.7
SB	1987	2780	75.9	1999	84.4
SB	1988	5950	95.4	3467	95.9
SB	1989	11033	85.2	9094	99.4
SB	1990	9419	98.1	4725	99.0
SB	1991	7025	84.0	4159	97.2
SB	1992	10925	94.4	8946	94.7
SB	1993	8854	98.6	5977	98.5
SB	1994	9987	98.1	8186	97.7
SB	1995	8883	99.1	5642	98.8
SD	1982	13072	96.4	8361	98.5
SD	1983	15835	97.6	11921	98.0
SD	1984	11296	69.2	9544	99.0

Table A4.2 [5/6] AOT40 values for forests and crops (forests Apr-Sept daylight hours, crops May-Jul daylight hours)

Site	Year	Forest	% dc Forest period	Wheat/Crops	%dc Wheat period
SH	1994	2583	95.6	2515	93.4
SH	1995	1223	44.5	1164	24.1
SO	1985	6038	66.5	3622	69.5
SO	1986	9890	65.0	8436	86.1
SO	1987	7078	37.5	3997	51.3
ST	1976	13102	12.7	13102	23.4
ST	1977	5574	93.7	3966	91.4
ST	1978	4066	92.5	3005	89.7
ST	1979	3033	90.8	1281	88.9
ST	1980	605	93.1	438	92.3
ST	1981	321	86.4	1	88.0
ST	1982	11305	75.7	10730	92.3
ST	1983	8100	89.3	5338	84.3
ST	1984	14925	97.9	9792	98.7
ST	1985	3510	94.1	2757	95.3
ST	1986	3499	65.4	2876	54.1
ST	1987	2052	85.7	1275	87.4
ST	1988	1315	96.2	613	99.3
ST	1989	3685	91.2	2920	90.2
ST	1990	6731	87.7	4012	78.6
ST	1991	1839	82.0	1247	93.6
ST	1992	4543	94.3	4131	99.6
ST	1993	2905	97.2	2506	95.8
ST	1994	1	14.0	---	0.0
SV	1987	3356	92.6	730	87.6
SV	1988	4742	96.3	3593	95.4
SV	1989	2852	67.9	2679	82.7
SV	1990	4646	96.1	3371	97.0
SV	1991	7739	91.5	4392	90.1
SV	1992	7316	94.2	5529	92.2
SV	1993	3980	85.4	2397	96.5
SV	1994	6351	83.5	4273	83.9
SV	1995	4753	96.1	2025	97.2
SW	1994	---	0.0	---	0.0
SW	1995	6079	94.4	3278	94.4
SY	1986	3285	91.8	3138	99.9
SY	1987	6871	97.7	3245	98.5
SY	1988	387	93.6	128	94.6
TD	1975	12151	82.7	7232	98.4
TD	1976	35598	77.8	25309	97.0
TD	1978	10258	71.3	8039	75.1
TD	1982	4325	57.4	2197	56.1
TD	1983	11435	60.3	9944	87.4
TD	1984	6818	71.0	5283	85.4
TD	1985	4093	59.7	2755	58.3
TD	1987	2153	42.1	1862	39.5
TD	1988	5249	50.5	6	26.4
TD	1989	9299	92.8	7403	93.9
TD	1990	7004	70.5	3983	64.3
TD	1991	3092	91.5	977	84.7
TH	1981	4272	99.9	1320	100.0
TH	1982	10254	97.2	8312	98.2
TH	1983	6601	96.1	4525	98.8
TH	1984	7994	97.3	4376	99.3
TH	1985	4094	97.0	3585	98.7
TH	1986	3923	99.8	3240	99.9
TH	1987	5828	94.1	3581	99.1
TH	1988	1892	81.8	864	74.3
WB	1981	---	0.0	---	0.0
WB	1982	6666	99.6	4495	99.8
WB	1983	4716	98.7	3547	99.2
WB	1984	---	0.0	---	0.0
WC	1985	1933	8.6	1933	15.7
WC	1986	479	20.6	479	17.0
WC	1987	1557	67.5	1524	66.7
WC	1988	3434	98.1	2460	98.6
WC	1989	5497	77.7	5231	72.6
WC	1990	5450	96.4	3523	98.5
WC	1991	9357	99.2	4689	98.9
WC	1992	5744	99.1	5124	98.5
WC	1993	5055	98.5	3356	99.1
WC	1994	4714	96.4	3911	98.4
WC	1995	10334	98.8	5564	99.7
WR	1985	4147	95.3	3211	93.5
WR	1986	1849	92.6	1449	96.4
WR	1987	3124	84.2	2289	83.1
WR	1988	---	0.0	---	0.0

Table A4.2 [6/6] AOT40 values for forests and crops (forests Apr-Sept daylight hours, crops May-Jul daylight hours)

Site	Year	Forest	% dc Forest period	Wheat/Crops	% dc Wheat period
WV	1995	---	0.0	---	0.0
YK	1986	---	0.0	---	0.0
YK	1987	576	36.2	314	33.2
YK	1988	112	99.0	92	99.8
YK	1989	239	54.9	238	45.3
YK	1990	309	98.9	154	98.1
YW	1987	905	45.6	829	28.4
YW	1988	3369	92.4	1669	89.7
YW	1989	15681	93.5	12410	90.1
YW	1990	15270	92.5	9724	97.6
YW	1991	11888	98.1	4561	97.2
YW	1992	11627	94.3	9718	95.5
YW	1993	5510	81.2	4134	94.6
YW	1994	6127	96.2	4869	95.2
YW	1995	13650	98.3	7279	99.6

See Table A4.3 for an index of site references.

Table A4.3 [1/6] Annual 8 Hour Running Mean Statistics

Site	Year	Periods ≥ 50 ppb	Days ≥ 50 ppb	Max	Median	%tile 97	%tile 97 of Daily Maxima	% dc
AH	1986	75	7	98.5	---	---	---	37.9
AH	1987	115	12	68	19.6	40.9	54.4	66.8
AH	1988	323	29	94.5	29.8	51.4	59.1	87.5
AH	1989	294	30	102.1	31.4	51.3	67.1	93.2
AH	1990	600	49	114.6	32.8	62.1	75	97.1
AH	1991	263	26	82	28.5	49.9	57.9	98.6
AH	1992	383	29	92	30.9	58.4	69.7	99.3
AH	1993	210	23	85.7	30.9	47	57.1	93.2
AH	1994	270	33	89	32.9	50.2	61.2	98.9
AH	1995	525	37	92.9	31.5	65.9	80.2	98.5
AS	1979	94	16	114.5	---	---	---	30.7
AS	1980	102	23	86.5	---	---	---	49.2
AS	1981	170	23	101	---	---	---	33.6
AS	1982	137	22	101.8	---	---	---	29.7
AS	1983	190	27	118.5	---	---	---	37.3
AS	1984	308	41	98.6	---	---	---	32.7
BA	1976	270	20	174.6	---	---	---	5.6
BC	1992	9	2	53.8	17.3	36.6	44.9	80.9
BC	1993	0	0	44.4	16	33.1	38.1	98.0
BC	1994	5	1	53	17.5	35.4	40.9	95.8
BC	1995	54	9	67.5	19	38	47.3	96.8
BH	1992	22	4	68.9	14.1	34.1	46.4	63.3
BH	1993	13	2	67.6	13.1	32.9	39.8	97.8
BH	1994	25	6	57.6	16.3	36.5	44.5	96.2
BH	1995	98	15	82.3	15.6	37.3	57.3	97.9
BO	1993	17	3	73.5	14.4	35	40.6	97.0
BO	1994	26	5	60.8	18.6	36.5	42.5	97.1
BO	1995	111	16	81.6	19	39.4	62.9	96.6
BP	1990	36	6	94	---	---	---	49.4
BP	1991	0	0	49.1	4.8	26.6	39	81.0
BP	1992	14	5	57.3	7.1	29.2	43.4	86.7
BP	1993	30	6	79.3	8.5	30	43.3	97.3
BP	1994	81	12	85.8	9.4	35.1	54.6	94.4
BP	1995	0	0	40.3	4.1	24.6	33.2	68.4
BR	1981	0	0	33.9	---	---	---	20.6
BR	1982	232	34	99.3	18.8	49.6	65.4	93.6
BR	1983	143	23	92	20.1	44.5	57	91.7
BR	1984	210	31	110.6	18.4	48.5	63.2	95.3
BR	1985	102	13	111.1	20.3	43.9	59.9	67.8
BS	1994	85	12	90	16.8	38.7	53	97.9
BS	1995	172	26	82.5	16	42.9	72.1	97.5
BT	1981	75	14	70.5	18.4	42.5	52.3	71.7
BT	1982	301	40	94.4	22	51.9	72.5	95.6
BT	1983	219	39	89.3	21.4	48.8	64.3	97.5
BT	1984	386	46	105	19.4	53.9	67.5	95.9
BT	1985	141	22	104.6	20.6	44.6	55.9	95.7
BT	1986	171	23	86.1	23.6	47	59.3	94.9
BT	1987	105	14	90.4	19	44.8	55.7	76.7
BT	1988	13	2	60.3	17	37.8	44.2	68.3
BT	1989	106	16	71.4	16.1	39.9	59.9	91.1
BT	1990	142	19	118	18.5	43.3	62.4	84.2
BT	1991	0	0	43.6	---	---	---	35.6
BT	1992	57	11	74.9	15.8	38.1	50.3	87.6
BT	1993	38	5	78.4	14.6	33.4	40.6	83.5
BT	1994	55	7	78	21	38.5	44.7	92.7
BT	1995	169	25	93.8	19	46.2	62.3	85.7

Table A4.3 [2/6] Annual 8 Hour Running Mean Statistics

Site	Year	Periods ≥ 50 ppb	Days ≥ 50 ppb	Max	Median	%tile 97	%tile 97 of Daily Maxima	%dc
BU	1986	20	4	61.3	24.4	37.8	42.4	87.2
BU	1987	75	9	88	22.8	41.3	49	96.6
BU	1988	116	14	70.6	27.9	44.3	51.4	97.0
BU	1989	139	18	89.5	27.5	44.5	57.6	98.6
BU	1990	155	17	92.6	27.9	45.1	54.5	97.8
BU	1991	17	3	71.3	25.1	37.9	44	99.6
BU	1992	145	15	71.1	27.6	46	53.4	98.8
BU	1993	0	0	48.9	26.4	40.3	45.7	97.0
BU	1994	46	8	68.9	28.8	43.6	47.3	98.9
BU	1995	54	5	76.5	24.9	40.4	45.5	81.3
CC	1992	110	18	92.6	10.5	45.4	62.3	61.3
CC	1993	62	9	76.7	12.8	36.4	45.7	95.9
CC	1994	50	8	93.5	15.5	37	47.1	97.1
CC	1995	200	25	95.4	16.3	45.3	72.2	96.9
CG	1979	91	15	83.3	---	---	---	28.1
CG	1982	106	17	83.8	---	---	---	21.0
CG	1983	101	18	93.9	---	---	---	39.2
CG	1984	121	16	134	---	---	---	15.8
CG	1985	77	12	76.8	---	---	---	14.4
CH	1975	203	24	139.6	---	---	---	41.7
CH	1976	261	30	178.8	---	---	---	29.3
CH	1978	5	1	63.8	---	---	---	18.1
CH	1979	125	16	110.4	---	---	---	32.8
CH	1980	45	7	84	---	---	---	30.1
CH	1981	67	11	87	---	---	---	45.8
CH	1982	26	5	62.8	---	---	---	26.1
CH	1983	146	20	83.5	---	---	---	22.5
CH	1984	80	9	79.4	---	---	---	22.0
CH	1985	107	18	79.1	---	---	---	29.6
CH	1986	102	14	96	---	---	---	29.1
CH	1989	172	25	100.9	---	---	---	35.7
CK	1974	11	2	62.4	---	---	---	37.8
CL	1972	126	19	97.4	---	---	---	32.8
CL	1973	360	42	115.1	12.1	63.3	87.1	72.1
CL	1974	218	34	121.7	14.3	50.3	65.3	80.5
CL	1975	71	15	76.3	6.7	40.1	56.9	76.2
CL	1976	255	30	113.8	10.3	54	74.4	74.2
CL	1977	38	5	86.1	---	---	---	47.9
CL	1978	141	24	99.4	9.6	45.3	63	81.9
CL	1979	36	8	72.6	8.1	33.5	48.9	73.1
CL	1980	13	2	65.3	8.1	31.5	41.5	60.8
CL	1981	28	5	96.9	---	---	---	56.3
CL	1982	12	3	54.9	8.6	28.3	38.1	63.5
CL	1983	2	1	51.3	---	---	---	39.5
CL	1984	12	3	55.8	---	---	---	22.6
CL	1985	244	33	112.9	11.9	50.6	66.9	86.6
CL	1986	82	12	80.4	7.4	35.8	55.3	75.4
CL	1987	14	4	58.2	---	---	---	39.4
CL	1988	3	1	53.6	6	24.3	31.9	89.5
CL	1989	97	15	81	6.9	36	58.7	95.3
CL	1990	43	6	74.8	9.5	32.4	46.4	60.8
CR	1973	18	3	72.4	2.4	23.5	37.6	62.2
CR	1974	0	0	29	---	---	---	38.0
CT	1986	0	0	34	---	---	---	1.3
CT	1987	34	9	74	---	---	---	27.0
CT	1988	1	1	57	---	---	---	58.4
CT	1989	176	23	115	27	45	66.4	88.7
CT	1990	232	32	96	28	48	68.1	94.8
CV	1977	785	64	128.3	---	---	---	44.7
CV	1978	462	44	128.1	13.3	55.5	73.9	74.2
CV	1979	121	23	80.6	13.5	44.3	59.7	87.4
CV	1980	12	2	63.5	---	---	---	46.0
CW	1975	751	71	141.9	---	---	---	47.5
DE	1978	62	11	73.7	19.1	39.1	50	98.5
DE	1979	0	0	46.5	18.1	32.5	38	94.7
DE	1980	26	4	59	16.6	35	45	85.0
DH	1992	573	32	79.7	27.8	63.5	72.5	68.4
DH	1993	145	9	85.3	29.8	46	49.6	93.2
DH	1994	231	19	72.9	31.9	48.8	54.2	99.8
DR	1987	0	0	29.3	---	---	---	26.6
DR	1988	12	2	64.1	16.8	34.3	40.5	94.8
DR	1989	344	38	98.5	22	53.7	68.5	95.8
DR	1990	300	32	113.4	18.4	51.6	73.7	77.0
ED	1992	0	0	30.1	---	---	---	24.3
ED	1993	0	0	37.9	11.5	28.5	33.5	95.6
ED	1994	0	0	48.4	13.8	31.6	37.2	96.0

Table A4.3 [3/6] Annual 8 Hour Running Mean Statistics

Site	Year	Periods ≥ 50 ppb	Days ≥ 50 ppb	Max	Median	%tile 97	%tile 97 of Daily Maxima	%dc
ED	1995	10	1	63.6	14.4	32.4	37.3	97.5
EK	1975	306	27	97.4	---	---	---	39.6
EM	1984	159	23	90.1	---	---	---	32.0
EM	1985	173	24	108.1	---	---	---	24.6
ES	1986	49	6	95.9	15.1	37	47.3	67.2
ES	1987	87	13	84	21	38	52	92.9
ES	1988	104	18	75	27	44	55.5	95.3
ES	1989	223	33	90	28	49	68.8	92.1
ES	1990	247	35	106	28	49	67.4	97.0
ES	1991	181	23	81	28	47	57.7	97.4
ES	1992	284	33	80	27	50	62.2	98.1
ES	1993	104	15	115	26	44	50.2	97.2
ES	1994	156	27	75	29	47	54.1	98.7
ES	1995	222	32	92	29	48	68.2	98.5
FL	1988	0	0	33.1	---	---	---	9.2
FL	1989	394	43	115.4	24.3	55.1	73.2	92.5
FL	1990	113	14	92.4	14.3	38.9	61.2	72.6
GD	1986	128	11	90.3	---	---	---	45.6
GD	1987	298	19	87.3	24.1	53.1	66.1	76.6
GD	1988	353	32	72.6	28.8	51.9	61.3	87.7
GD	1989	415	30	94	29	55.5	69.1	93.8
GD	1990	442	31	100.5	29.5	58.9	68.7	89.3
GD	1991	364	24	81.5	27.9	54.5	67.5	92.2
GD	1992	652	42	116.6	30	61.5	74.4	98.7
GD	1993	199	15	103.9	31	47.8	54.5	98.9
GD	1994	241	24	79.3	32.1	49.3	58.3	98.5
GD	1995	432	28	89.6	31	59.6	70.8	99.4
GL	1983	78	9	88.5	---	---	---	42.2
GL	1984	66	10	71.6	13.8	38.1	49.9	83.1
GL	1985	20	2	86.6	4.8	20.1	31.1	68.2
GL	1986	0	0	45.1	3.1	28.9	35.5	62.5
GZ	1989	59	10	75.4	11.6	38.5	51.4	79.6
GZ	1990	106	16	82.4	15.1	38.4	59.5	86.2
GZ	1991	69	15	64.6	11.8	43.9	54	77.8
GZ	1992	150	21	99.6	14.9	42.9	60.3	92.9
GZ	1993	43	9	75.9	14.5	38.1	47.2	99.3
GZ	1994	45	9	63.6	17.3	40	48.2	96.8
GZ	1995	135	19	83	15.9	40	64.8	94.6
HM	1987	0	0	46.6	---	---	---	44.3
HM	1988	208	22	69.5	23.9	48	55.8	97.3
HM	1989	321	25	91.1	24.1	53.2	74.2	89.3
HM	1990	310	25	101	25.6	52.3	64.3	94.8
HM	1991	390	35	76.3	27.6	52.6	61	99.3
HM	1992	474	33	90.6	26.4	58.1	67.4	85.0
HM	1993	180	19	101.7	25.5	48.1	54.2	80.4
HM	1994	231	26	87.1	28.9	49.1	56.1	99.1
HM	1995	328	27	89.5	28	54.4	63.7	96.8
HN	1975	211	23	108.6	---	---	---	29.2
HN	1976	628	64	152.3	---	---	---	28.1
HO	1979	9	3	64.4	---	---	---	36.4
HO	1980	17	5	56.8	---	---	---	50.2
HR	1976	341	18	217.3	---	---	---	4.8
HR	1983	269	27	112.3	---	---	----	33.4
HR	1984	419	43	94.3	21.9	55.8	75.7	83.3
HR	1985	322	37	91.3	25	51	59.2	91.3
HR	1986	131	13	113	21.9	41.4	55.6	92.8
HR	1987	74	11	80.7	17.3	40.3	52.2	82.0
HR	1988	26	5	67.5	17	37.8	48.1	64.4
HR	1989	256	32	104.5	10	49.5	76.9	65.3
HR	1990	341	40	110.9	24.6	54.4	72.3	95.0
HR	1991	252	38	81.6	25	49.5	69.1	98.6
HR	1992	366	42	104.4	23.5	55.4	78.6	87.0
HR	1993	136	16	88.9	19.1	45	62.3	76.1
HR	1994	234	36	99.6	24.6	48.8	67.4	91.2
HR	1995	360	38	96.9	24.3	56.4	79.6	91.1
HU	1994	19	2	86.5	14.6	35.3	41.8	98.1
HU	1995	29	6	68.8	14.9	35.8	43.3	96.8
HZ	1981	151	16	85.6	---	---	---	57.6
HZ	1982	60	6	61.3	---	---	---	21.8
IS	1976	185	32	117	---	---	---	28.0
IS	1977	108	23	127	5	41	60.3	75.5
IS	1978	43	14	98	---	---	---	33.3
JH	1984	187	34	86	15.5	47.5	58.7	85.9
JH	1985	86	14	85.3	18.5	41.5	51.7	94.4
JH	1986	129	22	79	20.1	45	54.1	84.5
JH	1987	286	37	103.4	18.3	50.9	75.5	88.3

Table A4.3 [4/6] Annual 8 Hour Running Mean Statistics

Site	Year	Periods ≥ 50 ppb	Days ≥ 50 ppb	Max	Median	%tile 97	%tile 97 of Daily Maxima	%dc
JH	1988	22	3	68.3	16.5	35.3	41.3	96.6
KW	1979	73	11	127	---	---	---	32.1
LB	1988	23	2	79.3	---	---	---	44.7
LB	1989	306	31	101	26.1	52	68.4	99.5
LB	1990	321	28	104.8	24.6	52.8	66.3	92.0
LB	1991	104	13	73.6	---	---	---	57.7
LB	1992	101	12	96.8	---	---	---	50.9
LB	1993	111	13	79.9	23.3	42.9	52.6	90.7
LB	1994	108	15	84	26.9	44.1	53.8	94.0
LB	1995	227	24	86.3	25	48.4	65.3	87.0
LC	1994	68	11	79.8	14.7	38.8	49.3	97.8
LC	1995	190	24	85.4	14.9	44.6	65.5	96.8
LD	1993	2	1	50.4	11	30.5	35.8	97.3
LD	1994	9	2	62.3	13.1	31.9	37.8	96.4
LD	1995	56	11	62.1	13.8	35.7	50	98.1
LH	1986	0	0	43.8	---	---	---	13.8
LH	1987	177	21	83.1	---	---	---	56.2
LH	1988	263	31	93.9	26.8	49.9	60	93.1
LH	1989	807	65	117.9	30	65.5	81.3	96.1
LH	1990	756	67	143.4	30.1	66.5	77.3	90.7
LH	1991	323	35	98.4	24.3	51.8	61.6	99.7
LH	1992	547	42	96.1	27	60.1	77.3	91.1
LH	1993	391	38	98	23.4	54.1	68.4	80.4
LH	1994	434	47	96.5	29.3	56	68.6	89.7
LH	1995	557	49	125.5	29.1	68	88.6	95.6
LN	1986	0	0	48.2	---	---	---	28.9
LN	1987	92	12	66.8	13.9	41.3	52.9	89.7
LN	1988	24	3	76.9	15.9	34.4	43.5	96.7
LR	1987	62	9	78.3	15.9	38.9	51.1	66.0
LR	1988	95	13	71.9	24.5	42.8	52.6	89.3
LR	1989	116	14	97.6	26.3	43.5	51	99.4
LR	1990	135	19	85.4	26.9	43.1	53.6	98.0
LR	1991	87	14	78.8	24.1	40.4	52.7	99.0
LR	1992	144	18	79.6	24.4	43.4	57.5	86.9
LR	1993	23	5	56.3	25.6	39.6	43.9	99.1
LR	1994	46	6	65.9	25.8	43.6	46.3	99.4
LR	1995	127	18	74	24	42.9	56.4	93.3
LV	1993	0	0	41.6	---	---	---	56.4
LV	1994	3	1	54.6	16.6	35.5	41.3	97.3
LV	1995	84	12	72.5	17	41.3	52.7	94.9
LY	1992	31	8	64.6	7.1	29.5	45.7	91.8
LY	1993	14	4	80.6	6.8	26	33.8	97.2
LY	1994	28	5	73.1	8.6	28.8	41.1	97.1
LY	1995	47	9	85.4	8.4	29.3	43.7	93.8
MD	1995	45	6	84.4	---	---	---	49.7
MH	1987	30	5	58.5	24.3	35.3	42.4	72.8
MH	1988	75	9	63.8	32.6	44.8	49	93.8
MH	1989	231	19	89.3	34.4	49.3	56.1	91.4
MH	1990	285	27	70.6	35.3	50.8	57.1	97.0
MH	1991	463	46	76	33.9	54.8	62.4	96.2
MH	1992	162	14	78.9	33.1	46.3	52.3	98.9
MH	1993	74	9	60.9	33.9	47.3	49.2	91.9
MH	1994	137	20	59.6	35.8	48.5	51.1	98.0
MH	1995	320	32	73.8	34.8	51.8	59.4	95.4
MP	1995	0	0	0	---	---	---	0.0
NC	1992	0	0	49.6	11.3	30.5	38.5	79.9
NC	1993	0	0	42.6	9.3	29.9	36.3	69.4
NC	1994	0	0	0	---	---	---	0.0
NC	1995	0	0	0	---	---	---	0.0
NN	1989	326	33	92.8	21.5	51.8	67.5	77.8
NN	1990	319	31	126.4	---	---	---	57.5
NW	1983	140	22	87.6	---	---	---	38.5
SB	1973	267	26	122.3	---	---	---	22.2
SB	1974	60	9	78.8	---	---	---	14.1
SB	1975	608	43	148.1	---	---	---	31.5
SB	1976	204	21	96.3	---	---	---	27.2
SB	1977	555	53	101.9	14.6	60.3	76.2	62.4
SB	1978	548	49	96.4	---	---	---	49.2
SB	1979	101	12	77.8	---	---	---	41.2
SB	1980	6	1	54.9	---	---	---	57.7
SB	1981	534	46	178	16.5	66.8	104.2	76.2
SB	1982	317	34	105.3	22.8	52	71.5	89.0
SB	1983	374	39	109.9	16.8	55	73.6	64.8
SB	1984	189	28	103.8	17	47.1	60.4	79.4
SB	1985	97	12	82.3	8.2	43.1	56.2	63.5
SB	1987	69	8	81.9	---	---	---	57.8

Table A4.3 [5/6] Annual 8 Hour Running Mean Statistics

Site	Year	Periods ≥ 50 ppb	Days ≥ 50 ppb	Max	Median	%tile 97	%tile 97 of Daily Maxima	%dc
SB	1988	220	26	85.8	23.1	48.1	60.7	88.4
SB	1989	431	46	107	22.3	55.5	73.6	91.3
SB	1990	341	39	126.5	24.4	53.2	70.4	97.0
SB	1991	281	38	75	17.8	50.4	63.1	66.2
SB	1992	477	42	109	24	57.9	72.3	95.2
SB	1993	425	40	106.1	26.3	53.4	62.4	99.2
SB	1994	377	42	109.8	24.4	53.1	68.7	95.8
SB	1995	287	32	96.4	25.4	51.4	66.1	97.6
SD	1982	588	56	101.6	21.5	59	77.2	72.6
SD	1983	756	92	136.9	31	57.4	71.8	97.0
SD	1984	353	47	114.4	---	---	---	53.7
SH	1994	55	10	77.4	16.5	38.3	49.6	97.7
SH	1995	28	4	85.1	9	33.3	41	73.5
SO	1985	212	22	131	---	---	---	40.9
SO	1986	356	39	106.1	---	---	---	38.0
SO	1987	286	30	128.7	---	---	---	17.1
ST	1976	298	21	186.4	---	---	---	5.6
ST	1977	160	25	111.1	12.6	46	59.5	66.2
ST	1978	139	21	84	13	43.2	55.5	93.4
ST	1979	71	12	85.1	10.9	34.3	50.8	82.3
ST	1980	14	2	66.8	7.6	26.9	37.3	85.8
ST	1981	6	1	59.9	5.3	18.5	26.2	85.2
ST	1982	313	28	118.9	10.6	54.2	96.5	73.9
ST	1983	239	31	119.5	13.6	48.9	73.9	73.5
ST	1984	486	57	152.8	15.6	58.2	76.9	88.6
ST	1985	120	17	102.4	11.3	40	56.6	78.4
ST	1986	161	21	95.5	---	---	---	56.9
ST	1987	54	9	69.5	5.1	31.9	50.8	69.5
ST	1988	26	5	58.4	9.5	33.5	45.3	89.5
ST	1989	108	13	83.8	8.8	37.3	61	86.2
ST	1990	147	20	113.5	11.6	42.3	66.6	92.2
ST	1991	59	8	74.8	9.1	34	46.1	90.2
ST	1992	136	19	81.9	8	40	63.7	80.3
ST	1993	97	9	103	13.1	37.6	45.5	98.4
ST	1994	0	0	40.1	---	---	---	31.7
SV	1987	113	8	81.1	26.5	44.8	50	71.4
SV	1988	196	18	66.5	33.8	48.6	54.5	96.7
SV	1989	63	8	71.8	29.8	44.6	49.3	79.1
SV	1990	195	22	73.1	32.3	48	54.1	88.8
SV	1991	335	40	69.4	31	51.2	58.2	90.1
SV	1992	363	24	71.3	33.9	54.3	61.9	96.4
SV	1993	111	13	62.2	32.3	47	51.2	81.9
SV	1994	250	24	69.8	33.1	49.8	57.2	74.3
SV	1995	192	21	84	34	47.6	54.8	96.1
SW	1994	0	0	38.3	---	---	---	8.5
SW	1995	200	27	92.1	18.4	44.9	68.7	97.3
SY	1986	102	15	88.3	14.3	42.3	53.5	66.6
SY	1987	233	22	112.6	21.6	48.7	71.1	90.1
SY	1988	10	1	61	17.4	32.4	38.3	93.5
TD	1975	310	39	110	---	---	---	33.5
TD	1976	886	87	180	---	---	---	41.0
TD	1978	237	28	120.3	---	---	---	36.7
TD	1982	112	19	93	---	---	---	28.2
TD	1983	303	44	107	---	---	---	28.5
TD	1984	197	28	87.3	---	---	---	40.2
TD	1985	101	15	83	---	---	---	29.6
TD	1987	54	8	108.5	---	---	---	42.9
TD	1988	409	44	100.9	7.6	56.6	76.3	61.4
TD	1989	242	37	93.9	13	48.6	76	71.7
TD	1990	200	28	109.1	13	45.3	74.7	74.9
TD	1991	78	15	68	12.3	37.6	54	81.8
TH	1981	119	16	84	10	45.3	60.5	72.1
TH	1982	280	33	97.2	17.6	51.2	74.9	96.3
TH	1983	175	26	85.3	20	46.4	61	96.9
TH	1984	244	37	95.3	18.4	49.3	59.9	97.2
TH	1985	141	18	88.5	18.6	44.2	56.1	93.4
TH	1986	108	15	84.1	21.3	42.5	53.1	96.1
TH	1987	172	19	92.3	17.3	45	64.4	87.7
TH	1988	37	5	91.4	13.3	37.7	46.4	82.4
WB	1981	0	0	25.9	---	---	---	24.9
WB	1982	192	28	89	16.9	46.2	64	98.8
WB	1983	115	19	83.9	19.1	43.1	55.6	98.3
WB	1984	0	0	37.8	---	---	---	10.7
WC	1985	111	10	87.3	---	---	---	4.0
WC	1986	29	3	68.6	---	---	---	32.1
WC	1987	60	6	80.1	16.3	37.1	43.4	74.1

Table A4.3 [6/6] Annual 8 Hour Running Mean Statistics

Site	Year	Periods ≥ 50 ppb	Days ≥ 50 ppb	Max	Median	%tile 97	%tile 97 of Daily Maxima	%dc
WC	1988	116	15	62.8	24	46.1	53	95.6
WC	1989	213	20	96.4	24.3	47.3	65.4	85.4
WC	1990	216	21	89.8	26	47.4	61.7	94.4
WC	1991	461	38	73.3	30.6	55.1	65	97.2
WC	1992	265	26	99.3	28.5	50.1	59.4	99.1
WC	1993	196	17	104.4	26.5	46.9	55.3	95.3
WC	1994	172	18	75.4	29.3	47.6	54.4	97.5
WC	1995	443	38	98	29.4	58.9	73.5	89.4
WR	1985	123	16	78.8	27.4	46	52.9	95.0
WR	1986	40	6	62.3	25.9	41.1	45.4	89.1
WR	1987	99	12	88	23.6	41.9	53.1	88.7
WR	1988	0	0	39.3	---	---	---	15.9
WV	1995	0	0	11.8	---	---	---	3.5
YK	1986	0	0	30.8	---	---	---	11.1
YK	1987	9	1	65.6	---	---	---	59.6
YK	1988	0	0	43.8	11.3	29.2	35.7	94.4
YK	1989	2	2	50.6	5.6	21.7	32.7	70.0
YK	1990	6	1	54	10.1	23.2	32.1	97.4
YW	1987	42	4	80	---	---	---	42.4
YW	1988	124	13	93.1	29.1	44.7	51.8	94.5
YW	1989	607	51	120.5	30.8	64.5	88.5	96.5
YW	1990	614	51	121.3	31.5	66	79	92.1
YW	1991	518	48	111.8	30.6	57	71	99.0
YW	1992	480	39	103	28.8	59.6	72.8	98.0
YW	1993	195	22	87.9	25.9	47.3	59.4	86.0
YW	1994	178	25	102.4	29.5	47.1	57.6	98.2
YW	1995	553	41	111.1	30.4	67.4	84.1	99.4

AH	Aston Hill	CL	Central London	GZ	Glazebury	SH	Southampton Centre
AS	Ascot	CR	Cromwell Road	HM	High Muffles	SO	St. Osyth
BA	St.Bartholomew's	CT	Clatteringshaws	HN	Hainault	ST	Stevenage
BC	Belfast Centre	CV	Canvey Island	HO	Harrow	SV	Strath Vaich
BH	Birmingham Centre	CW	Chilworth	HR	Harwell	SW	Swansea
BO	Bristol Centre	DE	Devilla	LY	London Bloomsbury	SY	Syda House
BP	Bridge Place	DH	Dunslair Heights	MD	Middlesbrough	TD	Teddington
BR	Brampton	DR	Dursley	MH	Mace Head	TH	Thorney
BS	Birmingham East	ED	Edinburgh Centre	MP	Manchester Piccadilly	WB	West Burton
BT	Bottesford	EK	East Kilbride	NC	Newcastle Centre	WC	Wharleycroft
BU	Bush	EM	East Malling	NN	North Norfolk	WR	Wray
CC	Cardiff Centre	ES	Eskdalemuir	NW	Nat West Tower	WV	Wolverhampton Centre
CG	Chigwell	FL	Fawley	SB	Sibton	YK	Yorkminster
CH	County Hall	GD	Great Dun Fell	SC	Sheffield Centre	YW	Yarner Wood
CK	Cardiff Kerbside	GL	Glasgow	SD	Stodday		

Median and percentile values are only given when data capture exceeds 60%.

Appendix 4:2 Annual Mean Ozone Map for the UK

As the mapping procedure cannot directly interpolate the annual averages but does give a map of the summer mean ozone, a relationship was derived for the annual to summer mean. A site average for the summer months, 1977-94, was calculated for every site on the PORG database and plotted against the sites annual average for the same period. This gave the linear relationship, *annual mean = 0.95.summer mean - 2.0,* with an R^2 coefficient of 0.93 indicating a good fit, see Figure A4.1 This equation was then applied to the map of summer mean produced using the average of 1990 - 94 data, see Figure A4.2. An urban correction was also calculated for a 5 km scale version of the map, using the method outlined in chapter 3, which gave the map shown in Chapter 7, Figure 7.21.

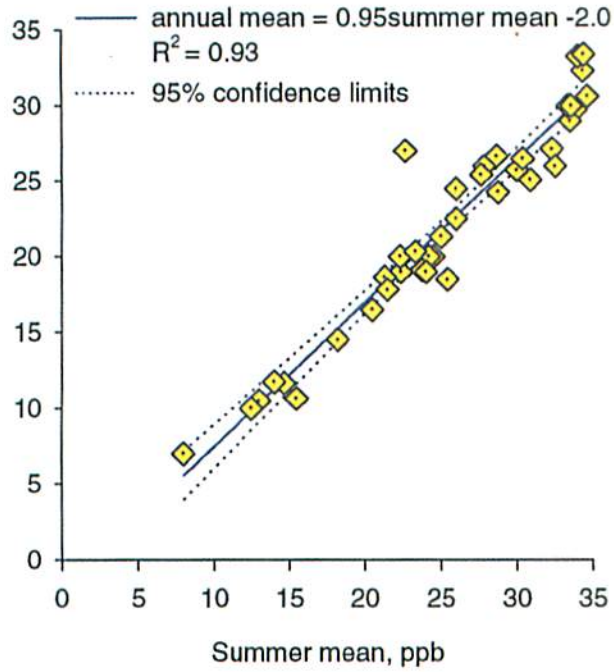

Figure A4.1 1977-94 summer vs. annual mean ozone for every site on the PORG database.

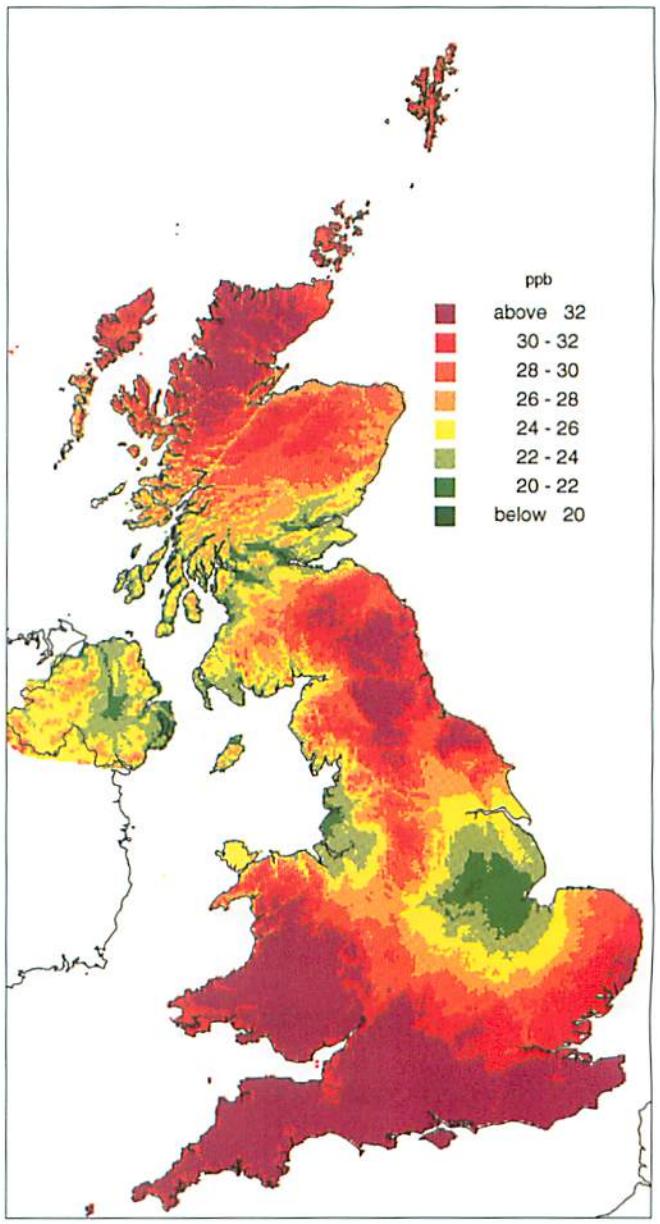

Figure A4.2 Annual mean ozone, based on 1990-94 summer mean values.

APPENDIX 5: TABLES OF NO_X AND NO_2 STATISTICS

Table A5.1 [1/3] Nitrogen Oxides Calendar Year Statistics, National Environmental Technology Centre: 15/08/96

Site	Year	Annual Mean (ppb)	50th %ile (ppb)	98th %ile (ppb)	Max. Hour (ppb)	Date of Max. Hour	Max. Run. 24 Hour (ppb)	No. of Hours >= 100 ppb	On No. of days	Stand. Dev. Geom.	Data Capture (%)
ST	77	54	43	176	529	25/10/77	18	45	23	1.9	70
ST	77	54	43	176	529	25/10/77	18	45	23	1.9	70
ST	78	55	42	222	587	30/11/78	29	93	35	2.1	74
ST	79	56	40	227	1039	05/10/79	138	100	29	2.1	70
ST	80	44	32	184	453	15/01/80	89	72	28	2.2	91
ST	81	59	43	240	660	06/11/81	14	144	42	2.4	85
ST	82	61	41	264	1270	03/12/82	92	187	57	2.3	89
ST	83	58	40	242	1423	04/11/83	62	132	37	2.3	80
ST	84	62	43	270	974	17/02/84	94	184	57	2.4	90
ST	85	49	37	211	703	13/11/85	40	64	18	2.4	49
ST	86	57	41	246	989	10/09/86	97	120	36	2.5	69
ST	87	73	51	325	932	12/04/87	50	166	37	2.3	55
ST	88	70	45	348	1055	06/11/88	85	305	71	2.6	89
ST	89	77	52	372	995	18/01/89	73	360	88	2.6	92
ST	90	69	52	271	939	16/10/90	120	203	64	2.3	92
ST	91	75	50	385	1075	08/12/91	35	376	77	2.4	98
ST	92	71	49	326	1002	17/02/92	20	322	76	2.6	98
ST	93	58	43	229	691	19/08/93	56	139	58	2.4	97
ST	94	56	41	230	659	12/04/94	49	45	16	2.3	32
CL	76	106	96	244	761	05/06/76	44	65	20	1.5	45
CL	77	105	94	246	1025	19/12/77	172	106	29	1.6	65
CL	78	89	79	236	562	22/12/78	38	103	28	1.7	69
CL	79	71	59	211	655	07/02/79	45	70	19	1.8	75
CL	80	63	53	191	583	16/02/80	50	41	11	1.7	63
CL	81	90	72	277	691	06/11/81	94	120	31	2.0	46
CL	82	94	75	282	1129	30/11/82	226	192	45	1.9	69
CL	83	80	64	266	1012	23/11/83	176	192	41	1.9	89
CL	84	77	65	215	520	01/10/84	84	78	26	1.7	78
CL	85	66	55	203	529	05/03/85	69	51	11	1.9	63
CL	86	73	61	222	665	28/11/86	126	96	23	1.8	84
CL	87	89	68	308	1062	11/12/87	189	236	37	2.0	87
CL	88	82	61	336	881	07/11/88	125	315	54	2.2	98
CL	89	85	64	338	1352	28/11/89	216	301	57	2.1	98
CL	90	65	56	179	615	08/01/90	87	35	11	1.9	62
CR	76	--	--	--	--	--	--	--	--	--	19
CR	77	197	160	614	1072	13/10/77	81	1020	142	2.0	45
CR	78	196	167	542	1696	17/08/78	45	915	133	1.9	42
CR	79	161	131	517	853	02/10/79	57	635	102	2.1	41
CR	80	--	--	--	--	--	--	--	--	--	11
CR	81	--	--	--	--	--	--	--	--	--	0
CR	82	231	186	742	2055	30/11/82	1817	2168	224	2.2	73
CR	83	279	217	898	2470	24/02/83	236	2610	237	2.2	70
CR	84	207	166	623	1128	10/11/84	76	1273	156	2.1	49
CR	85	202	165	583	1079	19/04/85	259	1260	151	2.3	49
CR	86	198	158	624	1230	09/12/86	104	1315	153	2.2	54
CR	87	--	--	--	--	--	--	--	--	--	0
CR	88	--	--	--	--	--		--	--	--	--
CR	89	267	220	806	2002	28/11/89	235	3057	268	2.2	80
CR	90	251	215	708	1418	14/12/90	82	3409	307	2.2	92
CR	91	273	234	783	1746	15/12/91	166	4014	340	2.1	99
CR	92	241	207	669	1087	30/12/92	93	3483	325	2.1	99
CR	93	217	193	559	1312	16/11/93	186	3007	320	2.1	100
CR	94	205	178	531	1172	23/12/94	224	2575	291	2.1	96
CR	95	206	180	545	1472	06/12/95	55	2393	285	2.0	92
GH	79	--	--	--	--	--	--	--	--	--	5
GH	80	--	--	--	--	--	--	--	--	--	20
GH	81	266	177	1162	1738	11/12/81	1181	1150	116	2.9	37
GH	82	208	142	810	1404	15/10/82	183	1833	231	2.7	73
HO	79	53	32	221	496	12/12/79	24	38	14	2.3	34
HO	80	46	33	176	711	01/02/80	135	54	15	2.0	70
SB	77	--	--	--	--	--	--	--	--	--	11
SB	78	10	8	31	86	21/02/78	42	0	0	1.8	42
SB	79	9	7	24	62	24/11/79	46	0	0	2.1	28
SB	80	--	--	--	--	--	--	--	--	--	0
SB	81	--	--	--	--	--	--	--	--	--	0
SB	82	--	--	--	--	--	--	--	--	--	0
SB	83	--	--	--	--	--	--	--	--	--	0
SB	84	--	--	--	--	--	--	--	--	--	0
SB	85	--	--	--	--	--	--	--	--	--	0
SB	86	--	--	--	--	--	--	--	--	--	0
SB	87	--	--	--	--	--	--	--	--	--	0
SB	88	--	--	--	--	--	--	--	--	--	23
SB	89	--	--	--	--	--	--	--	--	--	19

Table A5.1 [2/3] Nitrogen Oxides Calendar Year Statistics, National Environmental Technology Centre: 15/08/96

Site	Year	Annual Mean (ppb)	50th %ile (ppb)	98th %ile (ppb)	Max. Hour (ppb)	Date of Max. Hour	Max. Run. 24 Hour (ppb)	No. of Hours >= 100 ppb	On No. of days	Stand. Dev. Geom.	Data Capture (%)
IS	76	--	--	--	--	--	--	--	--	--	19
IS	77	56	44	175	509	25/03/77	21	34	18	1.9	72
IS	78	49	36	183	765	18/01/78	137	61	17	2.1	71
CV	77	--	--	--	--	--	--	--	--	--	21
CV	78	35	23	155	616	02/12/78	53	33	11	2.3	82
CV	79	28	20	110	244	02/10/79	26	0	0	2.3	60
CV	80	26	16	142	585	25/01/80	53	18	7	2.4	59
WL	87	95	68	377	1270	11/12/87	162	290	56	2.3	70
WL	88	100	68	456	1014	15/11/88	152	595	110	2.4	100
WL	89	123	81	596	1688	28/11/89	326	812	159	2.4	94
WL	90	82	65	270	1092	14/12/90	151	209	51	2.1	96
WL	91	94	69	361	1555	12/12/91	323	363	72	2.1	98
WL	92	83	60	373	847	30/12/92	142	354	62	2.3	99
WL	93	73	57	253	1042	16/11/93	148	176	44	2.2	98
WL	94	70	52	261	930	23/12/94	193	182	38	2.2	99
WL	95	64	49	233	667	31/10/95	73	138	38	2.1	98
GW	87	84	56	381	1013	01/12/87	167	416	70	2.4	91
GW	88	82	59	309	976	24/11/88	131	308	87	2.5	85
GW	89	82	51	426	1266	04/12/89	217	447	67	2.8	99
GW	90	79	52	370	1058	28/11/90	79	346	62	2.6	89
GW	91	88	58	383	1531	10/12/91	213	463	99	2.5	99
GW	92	81	56	362	937	31/01/92	94	386	79	2.5	99
GW	93	84	60	316	725	17/12/93	103	345	85	2.5	89
GW	94	69	49	272	986	22/12/94	132	236	60	2.4	98
GW	95	66	48	252	656	09/12/95	61	177	48	2.3	97
HR	95	--	--	--	--	--	--	--	--	--	12
LY	92	78	62	259	626	10/04/92	141	156	34	2.0	78
LY	93	72	60	213	784	16/11/93	108	91	21	2.0	94
LY	94	73	57	239	1208	23/12/94	207	151	31	2.0	96
LY	95	74	61	228	781	31/10/95	112	118	27	1.9	93
MT	87	69	45	329	1316	09/12/87	211	236	39	2.2	84
MT	88	69	44	361	1178	23/11/88	197	266	37	2.3	89
MT	89	68	43	316	1310	13/11/89	100	298	50	2.4	100
MT	90	63	47	239	1057	29/11/90	156	153	33	2.3	98
MT	91	62	46	223	791	22/01/91	105	129	35	2.1	99
MT	92	75	45	423	1587	23/12/92	369	413	47	2.4	97
MT	93	61	45	236	917	26/11/93	164	153	38	2.1	99
MT	94	63	42	292	1169	22/12/94	300	233	32	2.3	99
MT	95	49	33	219	1030	11/12/95	157	125	24	2.5	94
HU	94	54	40	202	1147	22/12/94	101	95	27	2.4	97
HU	95	54	40	186	649	11/12/95	57	57	15	2.3	98
WS	87	84	60	416	1069	28/11/87	87	233	42	2.2	61
WS	88	82	56	388	1190	31/10/88	95	374	69	2.3	90
WS	89	80	57	334	1682	13/11/89	148	330	79	2.4	94
WS	90	66	49	263	1284	05/12/90	153	198	45	2.2	95
WS	91	78	56	310	1089	01/02/91	76	329	74	2.1	99
WS	92	79	55	343	1622	23/12/92	191	321	62	2.2	97
WS	93	64	49	239	973	20/10/93	103	152	46	2.2	95
WS	94	61	44	236	1434	23/12/94	197	154	41	2.4	100
WS	95	65	43	315	951	11/12/95	115	201	41	2.4	78
BM	87	50	30	239	696	27/11/87	79	137	35	2.5	87
BM	88	42	26	184	712	25/11/88	127	71	27	2.6	94
BM	89	43	29	181	558	11/12/89	48	65	22	2.5	96
BM	90	42	25	195	683	22/11/90	103	91	26	2.5	91
BM	91	46	26	224	1045	14/01/91	84	120	29	2.7	99
BM	92	44	25	222	764	21/12/92	83	125	37	2.7	98
BM	93	36	21	167	563	26/11/93	57	60	21	2.8	94
BM	94	36	22	161	434	10/02/94	52	38	22	2.5	98
BM	95	37	28	136	321	19/09/95	58	7	7	2.1	71
SL	90	--	--	--	--	--	--	--	--	--	9
SL	91	93	67	388	1078	09/12/91	81	439	78	2.4	97
SL	92	104	74	500	1351	23/12/92	107	542	84	2.4	98
SL	93	81	60	282	1004	19/10/93	81	250	79	2.3	99
SL	94	81	62	292	995	22/12/94	89	274	59	2.4	97
SL	95	75	58	279	1087	11/12/95	111	192	55	2.4	83
BP	90	90	67	307	1021	14/12/90	150	146	35	2.0	49
BP	91	102	71	414	1567	13/12/91	423	495	82	2.2	99
BP	92	88	63	366	853	30/10/92	168	390	66	2.2	99
BP	93	73	56	250	997	16/11/93	140	175	44	2.2	99
BP	94	71	51	267	1018	23/12/94	268	205	43	2.2	99
BP	95	69	51	245	748	03/01/95	217	159	40	2.1	97
ED	92	--	--	--	--	--	--	--	--	--	24
ED	93	63	47	238	1032	26/11/93	114	148	50	2.2	95
ED	94	57	44	192	662	10/10/94	54	92	23	2.2	96
ED	95	57	43	216	608	12/12/95	71	109	27	2.2	92

Table A5.1 (3/3) Nitrogen Oxides Calendar Year Statistics, National Environmental Technology Centre: 15/08/96

Site	Year	Annual Mean (ppb)	50th %ile (ppb)	98th %ile (ppb)	Max. Hour (ppb)	Date of Max. Hour	Max. Run. 24 Hour (ppb)	No. of Hours >= 100 ppb	On No. of days	Stand. Dev. Geom.	Data Capture (%)
LH	88	--	--	--	--	--	--	--	--	--	18
LH	89	--	--	--	--	--	--	--	--	--	19
LH	90	--	--	--	--	--	--	--	--	--	21
LH	91	10	6	44	112	01/03/91	39	0	0	2.4	79
LH	92	9	6	45	311	02/02/92	90	4	1	2.5	85
LH	93	11	7	43	102	16/02/93	36	0	0	2.7	89
LH	94	10	6	42	101	11/11/94	33	0	0	2.5	69
LH	95	9	6	34	93	04/03/95	40	0	0	2.3	95
SV	90	--	--	--	--	--	--	--	--	--	17
SV	91	2	1	14	26	17/01/91	25	0	0	2.8	44
SV	92	1	1	5	14	23/01/92	13	0	0	2.1	85
SV	93	1	1	7	15	29/03/93	15	0	0	2.3	42
SV	94	1	1	9	23	19/02/94	22	0	0	2.7	68
SV	95	1	0	3	18	28/07/95	2	0	0	2.4	86
LB	88	--	--	--	--	--	--	--	--	--	14
LB	89	--	--	--	--	--	--	--	--	--	20
LB	90	--	--	--	--	--	--	--	--	--	11
LB	91	14	9	56	138	27/01/91	45	0	0	2.4	81
LB	92	11	8	46	137	14/01/92	43	0	0	2.5	95
LB	93	15	10	62	159	10/03/93	53	0	0	2.7	75
LB	94	10	7	47	150	13/10/94	28	0	0	2.6	87
LB	95	10	7	38	124	11/12/95	35	0	0	2.3	74
CC	92	54	39	219	716	20/11/92	66	88	28	2.4	62
CC	93	45	33	177	759	02/02/93	72	68	21	2.2	95
CC	94	45	30	195	829	08/05/94	242	111	40	2.4	96
CC	95	39	29	153	595	31/10/95	57	37	10	2.1	94
BC	92	48	30	239	955	22/12/92	97	96	23	2.8	61
BC	93	46	31	203	1173	26/11/93	186	113	33	2.6	97
BC	94	42	26	187	1309	22/12/94	85	88	25	2.6	95
BC	95	41	26	171	1343	11/12/95	182	96	24	2.6	95
BH	92	44	32	151	419	19/08/92	60	10	3	2.3	35
BH	93	49	35	176	597	29/08/93	262	40	16	2.5	94
BH	94	46	29	188	1206	22/12/94	136	80	14	2.5	96
BH	95	46	31	182	1016	11/12/95	177	86	18	2.3	97
NC	92	65	46	256	1046	21/12/92	95	138	54	2.7	73
NC	93	72	49	296	1076	26/11/93	99	275	120	2.7	96
NC	94	57	40	218	941	04/01/94	194	91	46	2.4	94
NC	95	44	33	163	548	14/11/95	57	33	15	2.2	93
LD	93	67	52	246	905	04/11/93	69	133	33	2.1	77
LD	94	70	52	265	1248	23/12/94	104	185	29	2.2	96
LD	95	64	49	240	711	04/11/95	74	154	40	2.2	97
BO	93	71	44	341	981	29/01/93	74	291	63	2.9	71
BO	94	62	37	310	1005	24/12/94	76	310	71	2.8	97
BO	95	63	37	308	807	31/10/95	77	295	78	2.7	97
LV	93	67	41	296	624	23/10/93	50	127	22	3.1	46
LV	94	58	38	244	701	14/12/94	77	157	33	2.8	97
LV	95	55	38	205	480	02/01/95	61	75	24	2.7	94
BS	93	--	--	--	--	--	--	--	--	--	8
BS	94	38	22	196	1272	23/12/94	189	103	20	2.4	97
BS	95	41	23	227	1133	11/12/95	158	143	27	2.5	97
LC	94	44	32	182	870	14/12/94	97	74	20	2.3	96
LC	95	45	32	186	863	10/12/95	106	86	18	2.2	96
SH	94	58	40	261	876	07/01/94	41	187	45	2.4	96
SH	95	58	42	236	732	06/11/95	78	106	35	2.4	73
LX	94	50	29	269	685	16/12/94	60	128	28	2.5	59
LX	95	45	29	226	694	03/01/95	78	138	32	2.4	96
SW	94	--	--	--	--	--	--	--	--	--	8
SW	95	52	34	201	790	13/01/95	90	63	26	2.8	96
MD	95	28	20	116	350	28/12/95	74	8	5	2.2	68
MP	95	--	--	--	--	--	--	--	--	--	0
SC	95	--	--	--	--	--	--	--	--	--	0
WV	95	--	--	--	--	--	--	--	--	--	4

Data for years with data capture >= 25% is displayed. See Table A5.2 for index of site names.

Table A5.2 (1/3) Nitrogen Dioxide Calendar Year Statistics, National Environmental Technology Centre: 15/08/96

Site	Year	Annual Mean (ppb)	50th %ile (ppb)	98th %ile (ppb)	Max. Hour (ppb)	Date of Max. Hour	Max. Run. 24 Hour (ppb)	No. of Hours >= 100 ppb	On No. of days	Stand. Dev. Geom.	Data Capture (%)
ST	77	23	21	52	102	06/04/77	53	1	1	1.7	70
ST	78	23	21	54	133	30/03/78	62	4	3	1.8	74
ST	79	25	22	70	156	29/11/79	99	38	9	1.9	71
ST	80	18	17	42	98	14/01/80	52	0	0	2.0	92
ST	81	18	17	50	120	05/09/81	65	6	3	2.2	86
ST	82	22	21	54	258	25/03/82	68	3	2	1.9	89
ST	83	20	18	47	96	23/10/83	45	0	0	2.1	80
ST	84	23	21	57	128	11/12/84	58	3	3	2.2	90
ST	85	25	23	57	88	01/03/85	55	0	0	2.1	49
ST	86	21	19	52	134	09/09/86	61	2	1	2.1	70
ST	87	27	24	72	162	30/11/87	92	15	7	1.8	55
ST	88	24	23	53	131	15/11/88	82	8	1	1.8	89
ST	89	25	23	56	139	19/01/89	97	15	4	1.8	92
ST	90	25	23	56	120	16/10/90	57	3	2	1.8	92
ST	91	24	23	52	108	13/12/91	72	2	1	1.7	98
ST	92	22	21	45	97	30/07/92	45	0	0	1.8	98
ST	93	21	20	45	74	13/02/93	50	0	0	1.8	97
ST	94	23	21	51	77	21/02/94	53	0	0	1.9	32
CL	76	48	45	97	198	07/05/76	110	67	19	1.5	48
CL	77	45	43	80	172	19/12/77	94	27	9	1.4	67
CL	78	39	36	77	136	01/06/78	101	22	6	1.4	69
CL	79	34	33	64	168	02/10/79	76	4	2	1.4	75
CL	80	33	32	66	121	16/04/80	83	11	4	1.5	63
CL	81	35	35	71	137	27/08/81	75	7	4	1.6	46
CL	82	43	39	110	272	30/09/82	146	199	33	1.7	69
CL	83	39	38	73	219	23/11/83	106	27	9	1.5	89
CL	84	43	42	81	156	19/06/84	81	35	16	1.4	78
CL	85	32	31	63	113	27/09/85	69	9	4	1.6	63
CL	86	35	35	65	178	14/10/86	84	15	4	1.6	84
CL	87	39	36	85	239	11/12/87	142	83	18	1.6	87
CL	88	35	34	74	176	06/11/88	111	51	11	1.6	98
CL	89	37	35	80	216	28/11/89	94	45	16	1.6	98
CL	90	35	34	75	114	03/08/90	83	8	3	1.6	62
CR	76	--	--	--	--	--	--	--	--	--	19
CR	77	43	36	127	242	26/10/77	130	197	35	1.9	45
CR	78	44	41	101	167	11/08/78	102	78	19	1.7	42
CR	79	36	33	82	165	29/11/79	95	33	11	1.6	41
CR	80	--	--	--	--	--	--	--	--	--	11
CR	81	--	--	--	--	--	--	--	--	--	0
CR	82	46	42	116	1817	30/11/82	340	252	66	2.3	73
CR	83	68	57	208	379	19/08/83	271	1095	124	2.1	70
CR	84	50	46	119	219	17/07/84	132	202	52	1.8	50
CR	85	48	43	128	259	19/04/85	172	251	41	2.0	49
CR	86	40	36	109	195	16/06/86	113	144	21	1.8	54
CR	87	--	--	--	--	--	--	--	--	--	0
CR	88	--	--	--	--	--	--	--	--	--	0
CR	89	45	42	105	271	28/11/89	163	186	39	1.6	80
CR	90	42	38	99	245	02/01/90	113	161	27	1.6	92
CR	91	43	38	103	382	13/12/91	236	204	32	1.6	99
CR	92	41	38	90	134	20/05/92	105	74	19	1.5	99
CR	93	40	39	81	186	16/11/93	113	38	9	1.5	100
CR	94	44	42	90	235	23/12/94	164	94	20	1.6	96
CR	95	47	44	101	170	05/05/95	123	178	33	1.5	92
GH	79	--	--	--	--	--	--	--	--	--	5
GH	80	--	--	--	--	--	--	--	--	--	20
GH	81	50	39	170	1181	11/12/81	182	274	42	2.3	37
GH	82	41	32	154	621	12/01/82	143	439	78	2.6	73
HO	79	24	22	55	117	02/10/79	56	3	1	1.8	34
HO	80	20	17	55	159	04/02/80	75	11	4	2.0	71
SB	77	--	--	--	--	--	--	--	--	--	11
SB	78	8	6	26	52	07/03/78	29	0	0	1.9	42
SB	79	5	3	19	46	24/11/79	22	0	0	2.3	28
SB	80	--	--	--	--	--	--	--	--	--	0
SB	81	--	--	--	--	--	--	--	--	--	0
SB	82	--	--	--	--	--	--	--	--	--	0
SB	83	--	--	--	--	--	--	--	--	--	0
SB	84	--	--	--	--	--	--	--	--	--	0
SB	85	--	--	--	--	--	--	--	--	--	0
SB	86	--	--	--	--	--	--	--	--	--	0
SB	87	--	--	--	--	--	--	--	--	--	0
SB	88	--	--	--	--	--	--	--	--	--	23
SB	89	--	--	--	--	--	--	--	--	--	19
IS	76	--	--	--	--	--	--	--	--	--	19
IS	77	26	26	57	107	04/08/77	55	2	1	1.9	72
IS	78	23	21	62	137	18/01/78	82	9	4	2.2	71

Table A5.2 [2/3] Nitrogen Dioxide Calendar Year Statistics, National Environmental Technology Centre: 15/08/96

Site	Year	Annual Mean (ppb)	50th %ile (ppb)	98th %ile (ppb)	Max. Hour (ppb)	Date of Max. Hour	Max. Run. 24 Hour (ppb)	No. of Hours >= 100 ppb	On No. of days	Stand. Dev. Geom.	Data Capture (%)
CV	77	--	--	--	--	--	--	--	--	--	22
CV	78	18	16	50	143	18/01/78	73	6	1	2.1	83
CV	79	16	14	41	74	10/09/79	48	0	0	2.1	60
CV	80	13	12	36	76	28/02/80	39	0	0	2.1	59
WL	87	35	32	84	271	30/11/87	137	61	12	1.8	70
WL	88	37	35	92	208	15/11/88	114	114	41	1.7	100
WL	89	42	38	112	363	06/06/89	193	241	59	1.7	94
WL	90	35	33	78	151	14/12/90	105	44	14	1.7	96
WL	91	35	33	73	388	13/12/91	235	78	8	1.6	98
WL	92	32	31	71	142	30/12/92	79	20	9	1.7	99
WL	93	31	31	64	155	16/11/93	86	12	2	1.7	98
WL	94	31	30	64	198	23/12/94	137	28	5	1.7	99
WL	95	28	27	64	131	05/05/95	79	12	4	1.7	98
GW	87	31	30	69	215	07/01/87	109	47	12	1.7	91
GW	88	30	30	57	131	24/11/88	66	7	2	1.8	85
GW	89	27	26	61	217	04/12/89	137	37	6	1.9	99
GW	90	26	25	53	114	07/12/90	61	4	2	1.8	89
GW	91	26	26	52	213	10/12/91	113	21	5	1.7	99
GW	92	25	25	50	94	31/01/92	51	0	0	1.8	99
GW	93	27	26	56	109	12/03/93	66	2	2	1.8	89
GW	94	26	26	50	132	22/12/94	81	4	2	1.8	98
GW	95	26	26	51	81	04/05/95	59	0	0	1.8	97
HR	95	--	--	--	--	--	--	--	--	--	12
LY	92	34	33	72	141	10/04/92	77	8	6	1.5	78
LY	93	34	34	63	120	09/06/93	83	7	3	1.5	94
LY	94	34	33	61	207	23/12/94	118	16	3	1.5	96
LY	95	35	34	71	176	05/05/95	100	36	8	1.5	93
MT	87	29	27	65	230	09/12/87	134	44	7	1.7	84
MT	88	28	26	67	256	25/11/88	179	66	7	1.8	89
MT	89	25	22	62	238	05/12/89	120	33	9	1.8	100
MT	90	28	24	74	191	30/04/90	117	41	13	1.9	98
MT	91	27	26	54	127	22/01/91	68	5	2	1.7	99
MT	92	31	28	78	369	23/12/92	159	93	13	1.8	97
MT	93	26	24	57	164	26/11/93	82	12	5	1.7	99
MT	94	25	20	80	352	22/12/94	222	119	12	1.9	99
MT	95	23	21	60	181	11/12/95	83	16	7	2.1	94
HU	94	24	24	51	111	29/11/94	55	4	3	1.9	97
HU	95	24	23	50	93	05/05/95	50	0	0	1.9	98
WS	87	30	29	62	104	28/11/87	75	2	1	1.6	61
WS	88	26	26	54	151	15/11/88	62	9	4	1.6	90
WS	89	29	29	59	214	13/11/89	102	15	6	1.7	94
WS	90	25	23	56	153	05/12/90	68	13	5	1.8	95
WS	91	26	25	54	137	11/12/91	66	5	3	1.6	99
WS	92	26	25	57	269	24/12/92	144	24	5	1.6	97
WS	93	24	24	47	118	19/10/93	57	3	2	1.7	95
WS	94	25	24	52	257	23/12/94	121	14	3	1.8	100
WS	95	24	23	53	119	10/12/95	83	6	4	1.9	78
BM	87	23	19	63	182	22/01/87	60	4	4	2.1	87
BM	88	21	18	58	212	01/07/88	68	13	6	2.2	94
BM	89	22	19	60	126	22/09/89	66	8	7	2.1	96
BM	90	21	17	62	125	22/11/90	69	15	8	2.1	91
BM	91	19	17	51	130	14/01/91	52	5	3	2.1	99
BM	92	18	16	49	143	26/03/92	52	1	1	2.2	98
BM	93	16	14	43	108	25/10/93	40	1	1	2.3	94
BM	94	16	14	44	112	18/03/94	41	1	1	2.1	98
BM	95	18	16	48	90	30/01/95	46	0	0	1.9	71
SL	90	--	--	--	--	--	--	--	--	--	9
SL	91	27	25	65	189	01/09/91	85	25	14	1.7	97
SL	92	31	29	73	179	22/07/92	91	34	15	1.7	98
SL	93	28	26	72	214	25/07/93	79	40	25	1.7	99
SL	94	28	27	64	148	07/02/94	66	10	10	1.7	97
SL	95	26	25	56	119	11/12/95	70	6	3	1.8	83
BP	90	37	36	90	150	14/12/90	111	51	10	1.7	49
BP	91	43	40	95	423	13/12/91	250	148	24	1.6	99
BP	92	39	36	90	175	10/04/92	99	95	26	1.7	99
BP	93	34	33	71	140	16/11/93	85	17	7	1.7	99
BP	94	34	32	79	268	23/12/94	174	70	12	1.8	99
BP	95	34	31	79	217	03/01/95	111	65	14	1.7	97
ED	92	--	--	--	--	--	--	--	--	--	24
ED	93	27	26	54	114	26/11/93	58	1	1	1.7	95
ED	94	26	27	51	91	21/08/94	53	0	0	1.8	96
ED	95	26	26	54	120	29/12/95	78	4	3	1.8	92
LH	88	--	--	--	--	--	--	--	--	--	18
LH	89	--	--	--	--	--	--	--	--	--	19
LH	90	--	--	--	--	--	--	--	--	--	21

Table A5.2 [3/3] Nitrogen Dioxide Calendar Year Statistics, National Environmental Technology Centre: 15/08/96

Site	Year	Annual Mean (ppb)	50th %ile (ppb)	98th %ile (ppb)	Max. Hour (ppb)	Date of Max. Hour	Max. Run. 24 Hour (ppb)	No. of Hours >= 100 ppb	On No. of days	Stand. Dev. Geom.	Data Capture (%)
LH	91	8	6	34	54	04/02/91	43	0	0	2.5	79
LH	92	7	5	32	90	02/02/92	43	0	0	2.6	85
LH	93	9	7	33	53	12/05/93	38	0	0	2.7	89
LH	94	9	6	33	64	18/02/94	53	0	0	2.5	69
LH	95	8	6	25	43	14/03/95	26	0	0	2.3	95
SV	90	--	--	--	--	--	--	--	--	--	17
SV	91	2	1	13	25	17/01/91	15	0	0	3.5	44
SV	92	1	0	5	13	23/01/92	8	0	0	2.5	85
SV	93	1	1	7	15	29/03/93	9	0	0	2.8	42
SV	94	1	0	8	22	19/02/94	11	0	0	3.2	68
SV	95	1	0	3	11	10/03/95	6	0	0	2.5	86
LB	88	--	--	--	--	--	--	--	--	--	14
LB	89	--	--	--	--	--	--	--	--	--	20
LB	90	--	--	--	--	--	--	--	--	--	11
LB	91	11	8	34	60	04/09/91	34	0	0	2.4	81
LB	92	9	7	32	57	26/02/92	40	0	0	2.5	95
LB	93	10	8	34	54	10/03/93	39	0	0	2.6	75
LB	94	9	6	33	62	22/02/94	40	0	0	2.6	87
LB	95	8	6	27	40	12/01/95	28	0	0	2.3	74
CC	92	25	24	49	79	14/09/92	45	0	0	1.8	62
CC	93	23	22	45	77	04/01/93	47	0	0	1.9	95
CC	94	22	21	48	264	08/05/94	56	15	9	1.9	96
CC	95	22	21	47	86	09/04/95	52	0	0	1.8	94
BC	92	23	21	58	130	19/05/92	61	4	4	2.3	61
BC	93	22	21	53	186	26/11/93	57	8	5	2.1	97
BC	94	21	19	47	100	16/02/94	66	1	1	2.1	95
BC	95	21	19	51	199	28/12/95	112	15	3	2.2	95
BH	92	24	22	59	127	28/09/92	60	1	1	2.0	35
BH	93	25	25	52	262	29/08/93	64	1	1	2.0	94
BH	94	24	22	55	136	22/12/94	77	8	3	2.1	96
BH	95	24	23	57	177	11/12/95	110	24	6	2.0	97
NC	92	27	26	62	285	13/04/92	55	8	8	2.1	73
NC	93	28	28	67	271	02/04/93	58	23	23	2.0	96
NC	94	24	23	55	204	04/01/94	57	12	9	1.9	94
NC	95	21	20	45	91	03/05/95	55	0	0	2.0	93
LD	93	26	26	49	83	30/06/93	50	0	0	1.6	77
LD	94	28	28	55	131	23/12/94	90	11	4	1.7	96
LD	95	26	26	53	109	21/08/95	65	1	1	1.8	97
BO	93	26	25	58	86	04/01/93	55	0	0	2.1	71
BO	94	24	22	56	91	24/12/94	60	0	0	2.0	97
BO	95	25	23	62	118	05/05/95	67	4	3	2.0	97
LV	93	27	26	59	108	30/04/93	61	2	1	2.2	46
LV	94	26	25	59	101	15/10/94	72	1	1	2.1	97
LV	95	26	25	58	90	03/05/95	69	0	0	2.2	94
BS	93	--	--	--	--	--	--	--	--	--	8
BS	94	20	18	48	189	23/12/94	102	9	2	2.0	97
BS	95	22	20	54	170	11/12/95	122	27	5	2.0	97
LC	94	23	22	47	97	14/12/94	60	0	0	1.8	96
LC	95	23	23	48	106	10/12/95	74	3	1	1.8	96
SH	94	23	22	51	81	20/12/94	53	0	0	1.8	96
SH	95	24	23	51	95	05/05/95	62	0	0	1.8	73
LX	94	22	21	51	106	23/12/94	65	1	1	1.9	59
LX	95	22	21	52	132	05/05/95	70	1	1	2.0	96
SW	94	--	--	--	--	--	--	--	--	--	8
SW	95	22	21	50	94	17/08/95	50	0	0	2.3	96
MD	95	17	15	42	97	29/06/95	41	0	0	2.1	68
MP	95	--	--	--	--	--	--	--	--	--	0
SC	95	--	--	--	--	--	--	--	--	--	
WV	95	--	--	--	--	--	--	--	--	--	4

Data for years with data capture >= 25 % is displayed.

BC Belfast Centre
BH Birmingham Centre
BM Billingham
BO Bristol Centre
BP Bridge Place, London
BS Birmingham East
CC Cardiff Centre
CL Central London
CR Cromwell Road
CV Canvey Island
ED Edinburgh Centre
GH Glasgow Hope St.
GW Glasgow City Chambers
HO Harrow
HR Harwell
HU Hull Centre
IS Islington
LB Ladybower
LC Leicester Centre
LD Leeds Centre
LH Lullington Heath
LV Liverpool Centre
LX London Bexley
LY London Bloomsbury
MD Middlesbrough
MP Manchester Piccadilly
MT Manchester Town Hall
NC Newcastle Centre
SB Sibton
SC Sheffield Centre
SH Southampton Centre
SL Sheffield Tinsley
ST Stevenage
SV Strath Vaich
SW Swansea
WL West London
WS Walsall
WV Wolverhampton Centre

Table A5.3 (1/3) Nitrogen Dioxide Exceedances of EC Directive Limit/Guide Values and UNECE Guidelines, NETCEN: 15/08/96

Site	Year	98th percentile >= 104.6 ppb	98th percentile >= 70.6 ppb	50th percentile >= 26.2 ppb	annual mean >= 50 ppb	Data Capture (%)
ST	77	52	52	21	23	70
ST	78	54	54	21	23	74
ST	79	70	70	22	25	71
ST	80	42	42	17	18	92
ST	81	50	50	17	18	86
ST	82	54	54	21	22	89
ST	83	47	47	18	20	80
ST	84	57	57	21	23	90
ST	85	57	57	23	25	49
ST	86	52	52	19	21	70
ST	87	72	72	24	27	55
ST	88	53	53	23	24	89
ST	89	56	56	23	25	92
ST	90	56	56	23	25	92
ST	91	52	52	23	24	98
ST	92	45	45	21	22	98
ST	93	45	45	20	21	97
ST	94	51	51	21	23	32
CL	76	97	97	45	48	48
CL	77	80	80	43	45	67
CL	78	77	77	36	39	69
CL	79	64	64	33	34	75
CL	80	66	66	32	33	63
CL	81	71	71	35	35	46
CL	82	110	110	39	43	69
CL	83	73	73	38	39	89
CL	84	81	81	42	43	78
CL	85	63	63	31	32	63
CL	86	65	65	35	35	84
CL	87	85	85	36	39	87
CL	88	74	74	34	35	98
CL	89	80	80	35	37	98
CL	90	75	75	34	35	62
CR	76	259	259	76	89	19
CR	77	127	127	36	43	45
CR	78	101	101	41	44	42
CR	79	82	82	33	36	41
CR	80	85	85	36	40	11
CR	81	--	--	--	--	0
CR	82	116	116	42	46	73
CR	83	208	208	57	68	70
CR	84	119	119	46	50	50
CR	85	128	128	43	48	49
CR	86	109	109	36	40	54
CR	87	--	--	--		
CR	88	--	--	--	--	0
CR	89	105	105	42	45	80
CR	90	99	99	38	42	92
CR	91	103	103	38	43	99
CR	92	90	90	38	41	99
CR	93	81	81	39	40	100
CR	94	90	90	42	44	96
CR	95	101	101	44	47	92
GH	79	61	61	25	27	5
GH	80	92	92	18	25	20
GH	81	170	170	39	50	37
GH	82	154	154	32	41	73
HO	79	55	55	22	24	34
HO	80	55	55	17	20	71
SB	77	32	32	5	7	11
SB	78	26	26	6	8	42
SB	79	19	19	3	5	28
SB	80	--	--	--	--	0
SB	81	--	--	--	--	0
SB	82	--	--	--	--	0
SB	83	--	--	--	--	0
SB	84	--	--	--	--	0
SB	85	--	--	--	--	0
SB	86	--	--	--	--	0
SB	87	--	--	--	--	0
SB	88	35	35	10	11.6	23
SB	89	17	17	6	6.7	19

Table A5.3 [2/3] Nitrogen Dioxide Exceedances of EC Directive Limit/Guide Values and UNECE Guidelines, NETCEN: 15/08/96

Site	Year	98th percentile >= 104.6 ppb	98th percentile >= 70.6 ppb	50th percentile >= 26.2 ppb	annual mean >= 50 ppb	Data Capture (%)
IS	76	99	99	26	31	19
IS	77	57	57	26	26	72
IS	78	62	62	21	23	71
CV	77	64	64	17	20	22
CV	78	50	50	16	18	83
CV	79	41	41	14	16	60
CV	80	36	36	12	13	59
WL	87	84	84	32	35	70
WL	88	92	92	35	37	100
WL	89	112	112	38	42	94
WL	90	78	78	33	35	96
WL	91	73	73	33	35	98
WL	92	71	71	31	32	99
WL	93	64	64	31	31	98
WL	94	64	64	30	31	99
WL	95	64	64	27	28	98
GW	87	69	69	30	31	91
GW	88	57	57	30	30	85
GW	89	61	61	26	27	99
GW	90	53	53	25	26	89
GW	91	52	52	26	26	99
GW	92	50	50	25	25	99
GW	93	56	56	26	27	89
GW	94	50	50	26	26	98
GW	95	51	51	26	26	97
HR	95	30.8	30.8	13.5	13.9	12
LY	92	72	72	33	34	78
LY	93	63	63	34	34	94
LY	94	61	61	33	34	96
LY	95	71	71	34	35	93
MT	87	65	65	27	29	84
MT	88	67	67	26	28	89
MT	89	62	62	22	25	100
MT	90	74	74	24	28	98
MT	91	54	54	26	27	99
MT	92	78	78	28	31	97
MT	93	57	57	24	26	99
MT	94	80	80	20	25	99
MT	95	60	60	21	23	94
HU	94	51	51	24	24	97
HU	95	50	50	23	24	98
WS	87	62	62	29	30	61
WS	88	54	54	26	26	90
WS	89	59	59	29	29	94
WS	90	56	56	23	25	95
WS	91	54	54	25	26	99
WS	92	57	57	25	26	97
WS	93	47	47	24	24	95
WS	94	52	52	24	25	100
WS	95	53	53	23	24	78
BM	87	63	63	19	23	87
BM	88	58	58	18	21	94
BM	89	60	60	19	22	96
BM	90	62	62	17	21	91
BM	91	51	51	17	19	99
BM	92	49	49	16	18	98
BM	93	43	43	14	16	94
BM	94	44	44	14	16	98
BM	95	48	48	16	18	71
SL	90	60	60	23	24	9
SL	91	65	65	25	27	97
SL	92	73	73	29	31	98
SL	93	72	72	26	28	99
SL	94	64	64	27	28	97
SL	95	56	56	25	26	83
BP	90	90	90	36	37	49
BP	91	95	95	40	43	99
BP	92	90	90	36	39	99
BP	93	71	71	33	34	99
BP	94	79	79	32	34	99
BP	95	79	79	31	34	97

Table A5.3 (3/3) Nitrogen Dioxide Exceedances of EC Directive Limit/Guide Values and UNECE Guidelines, NETCEN: 15/08/96

Site	Year	98th percentile >= 104.6 ppb	98th percentile >= 70.6 ppb	50th percentile >= 26.2 ppb	annual mean >= 50 ppb	Data Capture (%)
ED	92	48	48	29	28	24
ED	93	54	54	26	27	95
ED	94	51	51	27	26	96
ED	95	54	54	26	26	92
LH	88	38	38	8	11	18
LH	89	35	35	7	10.1	19
LH	90	23.5	23.5	3.7	5.9	21
LH	91	33.7	33.7	5.5	8.2	79
LH	92	31.5	31.5	4.9	7.4	85
LH	93	32.9	32.9	6.6	9.1	89
LH	94	33.1	33.1	5.5	8.5	69
LH	95	25.4	25.4	5.5	7.5	95
SV	90	7	7	0.3	0.9	17
SV	91	12.7	12.7	0.6	1.8	44
SV	92	4.5	4.5	0.3	0.7	85
SV	93	6.7	6.7	0.5	1	42
SV	94	8.3	8.3	0.3	1.1	68
SV	95	2.6	2.6	0.2	0.5	86
LB	88	50	50	10	14.1	14
LB	89	41	41	9	12.6	20
LB	90	33.2	33.2	10.7	12.6	11
LB	91	33.8	33.8	8.2	10.9	81
LB	92	32.1	32.1	6.7	9.1	95
LB	93	34.2	34.2	7.5	10.2	75
LB	94	33	33	6.2	8.8	87
LB	95	27	27	6.2	8.2	74
CC	92	49	49	24	25	62
CC	93	45	45	22	23	95
CC	94	48	48	21	22	96
CC	95	47	47	21	22	94
BC	92	58	58	21	23	61
BC	93	53	53	21	22	97
BC	94	47	47	19	21	95
BC	95	51	51	19	21	95
BH	92	59	59	22	24	35
BH	93	52	52	25	25	94
BH	94	55	55	22	24	96
BH	95	57	57	23	24	97
NC	92	62	62	26	27	73
NC	93	67	67	28	28	96
NC	94	55	55	23	24	94
NC	95	45	45	20	21	93
LD	93	49	49	26	26	77
LD	94	55	55	28	28	96
LD	95	53	53	26	26	97
BO	93	58	58	25	26	71
BO	94	56	56	22	24	97
BO	95	62	62	23	25	97
LV	93	59	59	26	27	46
LV	94	59	59	25	26	97
LV	95	58	58	25	26	94
BS	93	36	36	17	17	8
BS	94	48	48	18	20	97
BS	95	54	54	20	22	97
LC	94	47	47	22	23	96
LC	95	48	48	23	23	96
SH	94	51	51	22	23	96
SH	95	51	51	23	24	73
LX	94	51	51	21	22	59
LX	95	52	52	21	22	96
SW	94	57	57	23	23	8
SW	95	50	50	21	22	96
MD	95	42	42	15	17	68
MP	95	--	--	--	--	0
SC	95	--	--	--	--	0
WV	95	49	49	28	28	4

Data for years with data capture >= 25 % is displayed. See table A5.2 for index of site names.

Table A5.4 [1/3] Nitrogen Dioxide Exceedances of EC Directive Limit/Guide Values and UNECE Guidelines, NETCEN: 15/08/96

Site	Year	1 hour mean >= 210 ppb		daily mean >= 80 ppb	4 hour mean > = 50 ppb		annual mean >= 16 ppb	1 hour mean >= 104.6 ppb		Data Capture (%)
		count	days		count	days		count	days	
ST	77	0	0	0	123	26	23	0	0	70
ST	78	0	0	0	191	36	23	3	2	74
ST	79	0	0	2	295	40	25	34	8	71
ST	80	0	0	0	47	10	18	0	0	92
ST	81	0	0	0	129	25	18	3	2	86
ST	82	1	1	0	169	31	22	3	2	89
ST	83	0	0	0	57	22	20	0	0	80
ST	84	0	0	0	219	44	23	2	2	90
ST	85	0	0	0	191	28	25	0	0	49
ST	86	0	0	0	120	24	21	1	1	70
ST	87	0	0	1	337	42	27	9	5	55
ST	88	0	0	1	207	35	24	7	1	89
ST	89	0	0	1	227	45	25	13	3	92
ST	90	0	0	0	273	61	25	2	2	92
ST	91	0	0	0	186	32	24	2	1	98
ST	92	0	0	0	58	19	22	0	0	98
ST	93	0	0	0	67	14	21	0	0	97
ST	94	0	0	0	61	13	23	0	0	32
CL	72	4	4	7	1636	132	47	98	37	47
CL	73	10	4	12	1929	160	38	174	43	80
CL	74	0	0	5	489	42	28	53	8	83
CL	75	29	8	20	1820	123	54	230	41	42
CL	76	0	0	7	1826	128	48	51	15	48
CL	77	0	0	0	1821	174	45	23	8	67
CL	78	0	0	1	1017	103	39	19	5	69
CL	79	0	0	0	501	74	34	3	1	75
CL	80	0	0	0	424	59	33	6	3	63
CL	81	0	0	0	610	71	35	5	3	46
CL	82	10	3	14	1576	129	43	153	30	69
CL	83	1	1	1	1519	166	39	21	6	89
CL	84	0	0	0	1975	178	43	21	13	78
CL	85	0	0	0	404	61	32	5	3	63
CL	86	0	0	1	787	120	35	13	4	84
CL	87	2	1	4	1392	152	39	69	13	87
CL	88	0	0	3	1064	140	35	42	9	98
CL	89	1	1	1	1236	149	37	33	14	98
CL	90	0	0	0	666	75	35	6	3	62
CR	73	131	30	48	1795	117	52	707	93	57
CR	74	507	70	88	3445	207	89	1416	134	63
CR	75	362	61	74	2340	132	112	1261	103	34
CR	76	85	25	32	1261	76	89	538	64	19
CR	77	2	2	11	1119	103	43	159	31	45
CR	78	0	0	6	1189	103	44	60	16	42
CR	79	0	0	1	602	58	36	27	10	41
CR	80	0	0	0	192	22	40	8	3	11
CR	81	--	--	--	--	--	--	--	--	0
CR	82	22	9	18	2444	178	46	205	53	73
CR	83	121	23	67	3655	209	68	990	115	70
CR	84	2	2	8	2013	157	50	166	45	50
CR	85	7	3	15	1624	131	48	202	35	49
CR	86	0	0	10	1103	98	40	113	20	54
CR	87	--	--	--	--	--	--	--	--	0
CR	88	--	--	--	--	--	--	--	--	0
CR	89	10	1	14	2195	184	45	142	29	80
CR	90	1	1	13	2062	168	42	126	21	92
CR	91	22	3	12	2219	179	43	168	27	99
CR	92	0	0	8	2055	176	41	50	12	99
CR	93	0	0	2	1919	190	40	33	7	100
CR	94	8	1	7	2625	224	44	69	15	96
CR	95	0	0	11	2972	253	47	141	22	92
GH	79	0	0	0	21	3	27	2	1	5
GH	80	0	0	1	185	18	25	21	4	20
GH	81	39	17	18	1200	100	50	241	38	37
GH	82	22	12	22	1772	174	41	389	74	73
HO	79	0	0	0	90	14	24	1	1	34
HO	80	0	0	0	175	38	20	10	4	71
SB	77	0	0	0	0	0	7	0	0	11
SB	78	0	0	0	0	0	8	0	0	42
SB	79	0	0	0	0	0	5	0	0	28
SB	80	--	--	--	--	--	--	--	--	0
SB	81	--	--	--	--	--	--	--	--	0
SB	82	--	--	--	--	--	--	--	--	0
SB	83	--	--	--	--	--	--	--	--	0
SB	84	--	--	--	--	--	--	--	--	0

Table A5.4 (2/3) Nitrogen Dioxide Exceedances of EC Directive Limit/Guide Values and UNECE Guidelines, NETCEN: 15/08/96

Site	Year	1 hour mean >= 210 ppb		daily mean >= 80 ppb	4 hour mean > = 50 ppb		annual mean >= 16 ppb	1 hour mean >= 104.6 ppb		Data Capture (%)
		count	days		count	days		count	days	
SB	85	--	--	--	--	--	--	--	--	0
SB	86	--	--	--	--	--	--	--	--	0
SB	87	--	--	--	--	--	--	--	--	0
SB	88	0	0	0	0	0	12.0	0	0	23
SB	89	0	0	0	0	0	7.0	0	0	19
IS	76	0	0	2	228	23	31	31	7	19
IS	77	0	0	0	216	43	26	1	1	72
IS	78	0	0	1	298	56	23	8	4	71
CV	77	0	0	0	73	11	20	1	1	22
CV	78	0	0	0	124	33	18	6	1	83
CV	79	0	0	0	18	5	16	0	0	60
CV	80	0	0	0	8	3	13	0	0	59
WL	87	3	1	3	932	112	35	48	9	70
WL	88	0	0	6	1532	175	37	81	29	100
WL	89	26	10	12	2146	214	42	202	55	94
WL	90	0	0	3	1135	133	35	32	9	96
WL	91	16	3	5	982	128	35	73	7	98
WL	92	0	0	0	812	102	32	14	8	99
WL	93	0	0	0	597	93	31	10	2	98
WL	94	0	0	1	667	105	31	21	4	99
WL	95	0	0	0	476	60	28	10	4	98
GW	87	1	1	3	545	72	31	40	9	91
GW	88	0	0	0	423	70	30	6	2	85
GW	89	2	1	3	404	50	27	34	6	99
GW	90	0	0	0	192	32	26	3	2	89
GW	91	1	1	1	201	30	26	19	4	99
GW	92	0	0	0	163	29	25	0	0	99
GW	93	0	0	0	278	47	27	1	1	89
GW	94	0	0	0	159	31	26	3	2	98
GW	95	0	0	0	158	35	26	0	0	97
MT	87	3	1	4	423	59	29	38	6	84
MT	88	8	3	5	438	59	28	60	7	89
MT	89	2	1	1	390	54	25	27	7	100
MT	90	0	0	1	825	105	28	29	10	98
MT	91	0	0	0	256	66	27	4	2	99
MT	92	4	2	6	812	91	31	85	13	97
MT	93	0	0	0	291	45	26	9	4	99
MT	94	25	6	7	559	55	25	110	12	99
MT	95	0	0	0	348	56	23	13	6	94
WS	87	0	0	0	247	47	30	0	0	61
WS	88	0	0	0	232	48	26	5	2	90
WS	89	1	1	1	398	71	29	9	2	94
WS	90	0	0	0	319	55	25	9	4	95
WS	91	0	0	0	226	40	26	3	1	99
WS	92	5	1	1	272	43	26	20	4	97
WS	93	0	0	0	72	18	24	2	2	95
WS	94	1	1	1	209	34	25	13	3	100
WS	95	0	0	0	173	27	24	2	2	78
BM	87	0	0	0	397	68	23	3	3	87
BM	88	1	1	0	299	61	21	12	6	94
BM	89	0	0	0	281	65	22	4	3	96
BM	90	0	0	0	356	59	21	7	6	91
BM	91	0	0	0	134	27	19	4	3	99
BM	92	0	0	0	73	19	18	1	1	98
BM	93	0	0	0	13	8	16	1	1	94
BM	94	0	0	0	24	7	16	1	1	98
BM	95	0	0	0	37	12	18	0	0	71
SL	90	0	0	0	26	7	24	0	0	9
SL	91	0	0	1	490	89	27	18	11	97
SL	92	0	0	1	737	133	31	24	10	98
SL	93	1	1	0	585	109	28	33	22	99
SL	94	0	0	0	449	86	28	7	7	97
SL	95	0	0	0	222	43	26	4	2	83
BP	90	0	0	4	738	82	37	35	6	49
BP	91	23	4	7	2390	228	43	130	22	99
BP	92	0	0	7	1896	196	39	76	24	99
BP	93	0	0	0	1036	133	34	9	3	99
BP	94	8	1	4	1135	148	34	59	11	99
BP	95	1	1	5	922	123	34	45	10	97
ED	92	0	0	0	18	5	28	0	0	24
ED	93	0	0	0	220	48	27	1	1	95
ED	94	0	0	0	154	38	26	0	0	96
ED	95	0	0	0	203	31	26	3	2	92

Table A5.4 (3/3) Nitrogen Dioxide Exceedances of EC Directive Limit/Guide Values and UNECE Guidelines, NETCEN: 15/08/96

Site	Year	1 hour mean >= 210 ppb		daily mean >= 80 ppb	4 hour mean > = 50 ppb		annual mean >= 16 ppb	1 hour mean >= 104.6 ppb		Data Capture (%)
		count	days		count	days		count	days	
LH	88	0	0	0	0	0	11.0	0	0	18
LH	89	0	0	0	0	0	10.0	0	0	19
LH	90	0	0	0	0	0	5.9	0	0	21
LH	91	0	0	0	1	1	8.2	0	0	79
LH	92	0	0	0	7	1	7.4	0	0	85
LH	93	0	0	0	0	0	9.1	0	0	89
LH	94	0	0	0	17	2	8.5	0	0	69
LH	95	0	0	0	0	0	7.5	0	0	95
SV	90	0	0	0	0	0	0.9	0	0	17
SV	91	0	0	0	0	0	1.8	0	0	44
SV	92	0	0	0	0	0	0.7	0	0	85
SV	93	0	0	0	0	0	1.0	0	0	42
SV	94	0	0	0	0	0	1.1	0	0	68
SV	95	0	0	0	0	0	0.5	0	0	86
LB	88	0	0	0	21	6	14.0	1	1	14
LB	89	0	0	0	9	2	13.0	0	0	20
LB	90	0	0	0	0	0	12.6	0	0	11
LB	91	0	0	0	0	0	10.9	0	0	81
LB	92	0	0	0	4	2	9.1	0	0	95
LB	93	0	0	0	3	1	10.2	0	0	75
LB	94	0	0	0	5	2	8.8	0	0	87
LB	95	0	0	0	0	0	8.2	0	0	74
HR	95	0	0	0	0	0	13.9	0	0	12
LY	92	0	0	0	734	89	34	4	3	78
LY	93	0	0	0	640	90	34	5	2	94
LY	94	0	0	1	604	99	34	15	3	96
LY	95	0	0	3	858	108	35	26	7	93
CC	92	0	0	0	65	21	25	0	0	62
CC	93	0	0	0	63	19	23	0	0	95
CC	94	2	1	0	97	26	22	15	9	96
CC	95	0	0	0	73	20	22	0	0	94
BC	92	0	0	0	179	37	23	3	3	61
BC	93	0	0	0	185	40	22	7	4	97
BC	94	0	0	0	84	18	21	0	0	95
BC	95	0	0	0	143	29	21	15	3	95
BH	92	0	0	0	147	25	24	1	1	35
BH	93	1	1	0	200	44	25	1	1	94
BH	94	0	0	0	276	42	24	5	2	96
BH	95	0	0	2	303	46	24	21	6	97
NC	92	1	1	0	352	69	27	8	8	73
NC	93	1	1	0	562	118	28	15	15	96
NC	94	0	0	0	214	52	24	8	6	94
NC	95	0	0	0	56	18	21	0	0	93
LD	93	0	0	0	98	22	26	0	0	77
LD	94	0	0	0	298	53	28	7	3	96
LD	95	0	0	0	206	38	26	1	1	97
BO	93	0	0	0	260	57	26	0	0	71
BO	94	0	0	0	300	51	24	0	0	97
BO	95	0	0	0	484	70	25	3	2	97
LV	93	0	0	0	247	35	27	1	1	46
LV	94	0	0	0	434	58	26	0	0	97
LV	95	0	0	0	416	70	26	0	0	94
BS	93	0	0	0	0	0	17	0	0	8
BS	94	0	0	0	117	26	20	9	2	97
BS	95	0	0	2	210	34	22	24	4	97
HU	94	0	0	0	162	38	24	2	1	97
HU	95	0	0	0	122	26	24	0	0	98
LC	94	0	0	0	82	19	23	0	0	96
LC	95	0	0	0	130	23	23	1	1	96
SH	94	0	0	0	150	29	23	0	0	96
SH	95	0	0	0	120	26	24	0	0	73
LX	94	0	0	0	104	22	22	1	1	59
LX	95	0	0	0	169	30	22	1	1	96
SW	94	0	0	0	25	7	23	0	0	8
SW	95	0	0	0	96	28	22	0	0	96
MD	95	0	0	0	20	6	17	0	0	68
MP	95	--	--	--	--	--	--	--	--	0
SC	95	--	--	--	--	--	--	--	--	0
WV	95	0	0	0	0	0	28	0	0	4

Data for years with data capture >= 25 % is displayed. See table A5.2 for index of site names

APPENDIX 6: HYDROCARBON MEASUREMENTS IN THE UK

Appendix 6:1 Tables of network statistics

1. HR	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE		15.71	77.58		9.27	14.07		2.76	2.13		0.99	0.25
ETHENE		15.76	76.90		9.03	7.83		1.99	0.93		0.10	0.06
PROPANE		15.76	83.16		6.79	8.74		1.92	1.27		0.38	0.05
PROPENE		15.76	44.44		4.17	4.47		1.17	0.62		0.17	0.14
ETHYNE			43.44			30.84			2.79			0.14
iBUTANE			40.35			3.90			0.37			0.02
nBUTANE		15.76	83.11		10.86	14.50		1.55	0.95		0.15	0.02
t2BUTENE			6.85			0.60			0.23			0.14
1BUTENE			8.98			0.58			0.11			0.01
c2BUTENE			17.96			0.38			0.05			0.01
iPENTANE		15.74	82.53		8.07	11.00		1.03	0.67		0.06	0.02
nPENTANE		15.76	81.39		1.74	2.84		0.37	0.22		0.04	0.01
13BDIENE		15.74	78.87		0.87	1.11		0.17	0.07		0.02	0.01
t2PENTEN			5.71			1.21			0.05			0.01
c2PENTEN			4.77			0.60			0.03			0.00
MEPENT		15.65	72.22		3.38	4.30		0.38	0.21		0.02	0.01
ISOPRENE		13.54	4.54		0.52	0.24		0.06	0.05		0.01	0.01
nHEXANE		13.54	15.74		0.71	0.77		0.15	0.07		0.02	0.00
nHEPTANE		13.72	39.11		0.29	1.00		0.05	0.05		0.01	0.00
BENZENE		73.64	84.79		4.80	3.76		0.38	0.38		0.03	0.01
TOLUENE		66.28	78.40		43.42	50.47		0.65	0.60		0.03	0.02
ETHBENZ		22.98	27.95		1.61	1.12		0.18	0.16		0.01	0.01
mpXYLENE		24.84	29.36		3.80	2.96		0.45	0.38		0.04	0.02
oXYLENE		14.21	11.75		1.93	1.24		0.23	0.20		0.05	0.03

2. BL	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	8.55	90.29	86.90	27.20	83.88	33.12	3.49	4.63	3.89	0.80	0.36	0.70
ETHENE	8.53	90.55	86.87	21.10	54.32	49.85	2.25	2.64	3.00	0.10	0.08	0.12
PROPANE	62.91	92.02	93.26	71.40	50.43	35.33	2.03	2.47	2.30	0.10	0.23	0.18
PROPENE	63.04	91.89	85.03	14.30	37.18	19.36	1.70	1.82	1.82	0.20	0.19	0.20
ETHYNE	8.20	38.87	39.82	30.20	294.40	17.86	3.05	4.37	2.85	0.30	0.17	0.15
iBUTANE	63.15	38.98	40.54	49.50	73.48	32.11	2.05	1.56	0.83	0.00	0.07	0.05
nBUTANE	63.16	92.07	93.25	55.70	82.50	62.22	3.24	3.28	3.23	0.10	0.16	0.12
t2BUTENE	57.87	91.53	92.73	2.60	7.13	3.86	0.25	0.29	0.21	0.00	0.02	0.02
1BUTENE	55.17	90.81	91.77	2.50	6.68	5.35	0.19	0.22	0.18	0.00	0.01	0.01
c2BUTENE	55.41	90.32	90.76	1.90	5.14	3.25	0.16	0.18	0.14	0.00	0.01	0.01
iPENTANE	57.60	91.91	93.26	36.00	79.86	45.15	2.72	2.77	2.43	0.00	0.02	0.08
nPENTANE	55.29	90.74	93.25	12.40	17.89	14.18	0.87	0.69	0.71	0.00	0.01	0.03
13BDIENE	41.83	82.29	92.45	2.70	7.97	4.49	0.22	0.24	0.23	0.00	0.01	0.01
t2PENTEN	57.03	90.10	91.75	2.30	7.99	3.60	0.19	0.20	0.18	0.00	0.01	0.01
c2PENTEN	52.65	86.26	87.96	1.40	3.96	2.00	0.11	0.11	0.10	0.00	0.01	0.01
MEPENT	58.15	91.42	93.20	24.90	35.21	14.32	1.19	1.06	0.79	0.00	0.02	0.01
ISOPRENE	49.06	57.21	72.34	9.20	6.04	2.59	0.22	0.16	0.13	0.00	0.01	0.01
nHEXANE	56.18	57.21	80.90	4.90	5.56	3.45	0.31	0.23	0.18	0.00	0.01	0.01
nHEPTANE	55.15	86.94	92.96	3.30	4.18	2.85	0.17	0.16	0.13	0.00	0.00	0.01
BENZENE	62.72	93.03	93.74	13.70	31.30	21.37	1.06	1.22	1.22	0.00	0.07	0.07
TOLUENE	56.13	79.39	93.75	42.00	62.08	50.58	2.41	2.58	2.66	0.00	0.05	0.08
ETHBENZ	26.26	69.58	90.56	11.70	15.12	15.66	0.68	0.49	0.50	0.00	0.01	0.02
mpXYLENE	26.50	73.17	91.53	16.60	48.25	48.73	1.28	1.55	1.47	0.00	0.09	0.03
oXYLENE	29.52	55.17	52.25	3.90	14.58	15.13	0.40	0.61	0.67	0.00	0.04	0.02

3. LE	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	82.80	88.01	92.78	42.60	46.52	34.28	3.76	4.13	4.18	0.00	0.44	0.76
ETHENE	81.77	88.16	92.77	49.20	47.81	55.45	3.51	3.59	3.38	0.00	0.04	0.12
PROPANE	87.31	88.20	92.94	21.80	20.95	27.20	1.81	1.94	2.04	0.00	0.08	0.16
PROPENE	87.84	88.21	92.94	17.80	16.45	23.45	1.55	1.38	1.36	0.00	0.11	0.16
ETHYNE	62.00	69.39	89.95	75.30	45.36	91.13	4.09	3.60	4.61	0.00	0.18	0.19
iBUTANE	67.74	69.42	89.72	54.80	47.67	19.70	2.57	1.85	1.38	0.00	0.07	0.07
nBUTANE	87.82	88.24	92.94	59.10	52.28	66.99	3.72	3.59	3.23	0.00	0.07	0.14
t2BUTENE	79.81	87.19	89.34	3.10	3.53	4.45	0.25	0.24	0.21	0.00	0.01	0.03
1BUTENE	73.31	85.79	88.88	3.30	3.00	5.16	0.22	0.22	0.20	0.00	0.01	0.02
c2BUTENE	72.67	85.58	87.66	2.60	2.42	3.16	0.17	0.14	0.12	0.00	0.01	0.01
iPENTANE	86.96	87.69	92.78	65.40	43.00	49.99	2.88	2.93	2.57	0.00	0.07	0.08
nPENTANE	88.04	87.67	92.92	10.50	9.26	9.42	0.75	0.62	0.56	0.00	0.02	0.02
13BDIENE	71.89	87.09	92.60	3.50	3.48	4.76	0.24	0.24	0.21	0.00	0.01	0.01
t2PENTEN	75.24	86.44	87.98	4.30	2.75	3.45	0.22	0.16	0.13	0.00	0.01	0.01
c2PENTEN	71.92	81.89	80.19	2.20	1.46	1.89	0.12	0.09	0.08	0.00	0.01	0.00
MEPENT	89.89	88.20	92.86	19.50	17.16	21.76	1.30	1.16	0.95	0.00	0.02	0.03
ISOPRENE	54.92	75.24	91.51	2.00	1.37	2.00	0.16	0.12	0.14	0.00	0.01	0.00
nHEXANE	88.93	75.24	91.51	4.50	4.51	8.44	0.37	0.25	0.24	0.00	0.01	0.01
nHEPTANE	75.42	88.21	93.55	3.40	1.32	1.96	0.16	0.11	0.10	0.00	0.00	0.01
BENZENE	83.39	91.16	94.27	13.50	15.29	18.68	1.14	1.02	1.06	0.00	0.04	0.08

TOLUENE	77.81	87.44	94.29	40.90	37.37	47.04	2.42	2.13	2.16	0.00	0.05	0.07
ETHBENZ	41.04	67.59	86.76	5.40	8.11	8.76	0.47	0.41	0.37	0.00	0.02	0.01
mpXYLENE	48.13	68.38	87.02	27.20	25.95	26.78	1.28	1.19	1.02	0.00	0.04	0.02
oXYLENE	64.59	48.20	72.10	11.30	8.94	10.39	0.45	0.52	0.43	0.00	0.02	0.01
4. BF	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	96.15	95.45	92.74	15.50	21.32	17.36	1.38	2.38	2.17	0.00	0.48	0.35
ETHENE	95.71	95.38	92.70	42.70	83.40	52.20	1.67	2.84	2.26	0.00	0.04	0.04
PROPANE	95.65	95.08	92.74	296.80	3297.00	1229.00	6.23	14.39	12.71	0.00	0.55	0.49
PROPENE	96.44	95.09	92.70	28.80	62.11	23.57	1.05	1.15	0.97	0.00	0.11	0.10
ETHYNE	93.77	54.79	89.83	64.00	91.24	88.22	2.52	2.71	3.73	0.10	0.10	0.13
iBUTANE	96.43	54.81	89.65	58.40	159.30	72.91	1.69	1.56	1.11	0.00	0.07	0.04
nBUTANE	96.32	95.05	92.74	90.10	254.70	219.70	3.43	3.14	2.82	0.10	0.10	0.08
t2BUTENE	96.42	65.62	90.56	4.70	5.30	7.90	0.24	0.16	0.14	0.00	0.00	0.01
1BUTENE	95.61	92.95	87.64	6.80	7.55	8.18	0.21	0.17	0.15	0.00	0.01	0.01
c2BUTENE	95.91	64.50	81.59	3.70	4.11	5.77	0.14	0.12	0.10	0.00	0.01	0.01
iPENTANE	96.34	94.91	92.71	51.60	121.30	71.07	1.91	1.60	1.43	0.10	0.04	0.04
nPENTANE	96.36	95.06	92.74	20.90	47.41	25.43	0.78	0.63	0.59	0.00	0.02	0.02
13BDIENE	95.27	94.01	88.05	5.50	6.49	4.73	0.18	0.17	0.16	0.00	0.01	0.01
t2PENTEN	95.30	91.91	81.74	6.40	7.56	3.29	0.14	0.11	0.10	0.00	0.00	0.01
c2PENTEN	84.26	82.96	70.53	3.40	3.51	1.56	0.07	0.06	0.05	0.00	0.00	0.01
MEPENT	95.84	94.67	91.73	27.30	30.23	18.41	0.97	0.71	0.52	0.00	0.02	0.01
ISOPRENE	86.70	56.32		2.80	1.80		0.11	0.07		0.00	0.00	
nHEXANE	96.21	56.32	62.41	6.50	10.59	10.50	0.24	0.22	0.18	0.00	0.01	0.01
nHEPTANE	96.10	93.20	92.09	3.80	4.33	7.17	0.17	0.16	0.13	0.00	0.01	0.01
BENZENE	96.78	95.14	93.01	26.30	34.02	23.60	1.10	0.90	0.92	0.00	0.04	0.05
TOLUENE	96.54	82.59	92.79	58.70	81.84	52.61	2.18	1.78	1.76	0.00	0.04	0.05
ETHBENZ	89.71	64.51	85.06	9.90	14.76	10.07	0.40	0.45	0.36	0.00	0.04	0.02
mpXYLENE	93.39	66.78	88.46	34.20	45.02	30.49	1.27	1.32	1.01	0.00	0.10	0.03
oXYLENE	55.40	54.18	66.78	9.30	17.79	11.00	0.41	0.57	0.42	0.00	0.05	0.02
5. LU	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	90.22	89.69	93.58	15.40	42.08	36.07	1.91	4.12	3.38	0.30	0.83	0.58
ETHENE	90.23	89.70	93.58	33.50	33.83	36.64	2.42	3.45	3.47	0.10	0.23	0.20
PROPANE	90.14	89.71	93.74	71.30	36.97	31.91	2.62	2.72	2.56	0.40	0.38	0.38
PROPENE	90.50	89.73	93.74	30.00	22.25	30.75	2.40	2.21	2.06	0.20	0.24	0.28
ETHYNE	90.05	28.71	86.58	93.70	73.27	108.20	9.30	6.98	7.05	0.50	0.38	0.47
iBUTANE	90.45	28.95	86.58	43.70	34.38	37.59	3.50	4.60	2.63	0.20	0.40	0.17
nBUTANE	90.49	89.69	93.83	76.30	130.30	93.98	6.46	5.76	4.93	0.40	0.41	0.34
t2BUTENE	90.47	89.01	93.64	6.70	4.78	4.82	0.36	0.36	0.28	0.00	0.04	0.03
1BUTENE	90.48	89.53	93.69	13.00	4.74	5.65	0.40	0.35	0.31	0.00	0.03	0.02
c2BUTENE	90.38	89.59	93.25	9.60	3.25	4.30	0.29	0.23	0.21	0.00	0.01	0.01
iPENTANE	90.46	89.73	93.83	56.60	73.90	70.06	4.88	4.27	4.06	0.20	0.23	0.23
nPENTANE	90.49	89.71	93.80	17.40	11.48	11.80	1.24	0.96	0.95	0.10	0.06	0.06
13BDIENE	90.29	89.73	93.77	8.80	2.62	5.21	0.38	0.35	0.38	0.00	0.02	0.02
t2PENTEN	90.33	89.66	93.66	14.70	4.65	4.49	0.40	0.25	0.27	0.00	0.01	0.01
c2PENTEN	90.05	88.42	93.35	12.00	2.79	2.88	0.21	0.12	0.15	0.00	0.01	0.01
MEPENT	90.50	89.62	91.66	26.50	24.21	24.63	1.72	1.48	1.69	0.00	0.05	0.05
ISOPRENE	82.35	65.31	12.17	5.30	3.57	2.00	0.29	0.26	0.26	0.00	0.01	0.02
nHEXANE	90.20	65.31	72.63	24.80	4.26	5.08	0.53	0.28	0.43	0.00	0.01	0.03
nHEPTANE	78.07	88.28	84.88	31.20	3.69	3.75	0.25	0.18	0.23	0.00	0.01	0.01
BENZENE	90.80	90.95	94.48	24.30	18.67	26.01	1.78	1.69	1.87	0.10	0.14	0.13
TOLUENE	89.28	74.22	93.29	55.70	39.89	52.13	3.59	3.46	3.62	0.00	0.12	0.21
ETHBENZ	61.76	67.65	84.03	36.00	9.44	12.15	0.71	0.74	0.73	0.00	0.03	0.03
mpXYLENE	74.66	75.82	82.50	49.10	31.33	41.68	2.02	2.36	2.14	0.00	0.10	0.09
oXYLENE	89.34	74.46	69.87	22.00	8.61	12.80	0.89	0.86	0.80	0.00	0.04	0.03
6. LS	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE		61.07	87.52		48.44	42.09		6.12	3.28		1.31	0.06
ETHENE		61.07	87.74		34.57	33.07		3.87	1.84		0.30	0.04
PROPANE		61.07	88.37		43.83	103.70		4.21	3.04		0.72	0.02
PROPENE			26.50			23.39			1.87			0.30
ETHYNE		60.59	80.71		67.90	131.00		8.49	3.62		0.52	0.13
iBUTANE		60.59	81.15		20.61	56.10		2.41	1.52		0.31	0.04
nBUTANE		61.07	88.33		43.19	248.30		4.55	3.58		0.55	0.07
t2BUTENE			34.63			11.70			0.53			0.08
1BUTENE		59.56	78.90		2.80	16.60		0.31	0.23		0.02	0.01
c2BUTENE			74.57			7.59			0.22			0.02
iPENTANE		61.07	88.33		25.29	206.50		2.83	2.10		0.24	0.04
nPENTANE		61.07	88.32		63.07	65.48		1.02	0.99		0.10	0.02
13BDIENE		61.00	87.93		3.34	28.95		0.35	0.21		0.02	0.01
t2PENTEN		60.79	84.80		2.75	6.26		0.23	0.13		0.01	0.01
c2PENTEN		59.90	77.88		1.35	3.40		0.12	0.07		0.00	0.00
MEPENT		60.66	88.30		9.93	26.51		1.29	0.90		0.16	0.04
ISOPRENE		13.05			1.55			0.28			0.03	
nHEXANE		13.05	80.89		4.43	16.39		1.19	1.00		0.49	0.11
nHEPTANE		55.67	88.00		2.57	4.17		0.28	0.16		0.06	0.01

BENZENE		61.20	90.87		10.63	14.28		1.64	0.89		0.20	0.03
TOLUENE		61.20	90.69		55.28	55.10		3.36	2.08		0.23	0.09
ETHBENZ		60.45	84.89		56.18	78.01		1.61	0.87		0.03	0.02
mpXYLENE		60.45	86.05		162.90	306.70		4.98	2.68		0.09	0.04
oXYLENE		43.37	41.25		49.52	77.92		2.01	1.30		0.06	0.04
7. SH	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE		83.30	91.52		75.62	180.80		5.08	3.41		0.85	0.60
ETHENE		83.30	91.48		28.40	36.64		3.87	2.70		0.15	0.09
PROPANE		83.33	91.54		227.70	591.00		3.89	3.21		0.18	0.15
PROPENE		83.33	46.98		27.18	27.27		2.59	3.26		0.29	0.33
ETHYNE		51.43	49.29		108.90	146.70		9.12	4.71		0.66	0.23
iBUTANE		51.26	49.06		61.34	105.60		6.52	3.32		0.76	0.04
nBUTANE		83.30	91.54		75.94	369.60		6.15	4.54		0.15	0.08
t2BUTENE		83.23	91.54		8.53	4.90		0.53	0.35		0.06	0.07
1BUTENE		82.41	91.02		6.24	10.79		0.45	0.30		0.02	0.01
c2BUTENE		83.09	91.53		6.02	3.65		0.36	0.21		0.02	0.02
iPENTANE		83.33	91.52		80.30	103.10		5.34	3.49		0.16	0.09
nPENTANE		83.27	91.54		42.56	125.20		1.56	1.17		0.05	0.03
13BDIENE		83.30	91.51		5.56	19.39		0.50	0.36		0.01	0.02
t2PENTEN		82.55	91.19		6.99	7.31		0.41	0.26		0.01	0.01
c2PENTEN		82.48	90.64		3.65	3.86		0.20	0.13		0.01	0.01
MEPENT		83.30	90.98		36.38	40.45		2.25	1.49		0.04	0.01
ISOPRENE		67.01	34.05		2.19	1.96		0.22	0.14		0.01	0.01
nHEXANE		67.04	85.79		7.77	32.10		0.74	0.51		0.01	0.01
nHEPTANE		83.88	91.76		3.41	8.99		0.29	0.22		0.01	0.01
BENZENE		83.95	92.38		27.80	33.65		2.46	1.92		0.10	0.09
TOLUENE		83.98	92.37		55.21	64.51		4.78	3.60		0.16	0.09
ETHBENZ		83.27	90.57		10.50	16.43		0.95	0.67		0.03	0.02
mpXYLENE		83.30	90.54		33.11	67.35		2.93	2.05		0.10	0.04
oXYLENE		64.31	64.24		12.38	19.25		1.08	0.75		0.04	0.03
8. BS	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	90.62	95.91	81.00	71.20	89.89	98.93	5.01	5.13	6.72	0.00	0.05	0.28
ETHENE	90.70	96.63	80.61	66.00	61.29	89.91	2.88	2.61	3.21	0.10	0.02	0.12
PROPANE	91.36	96.88	82.84	60.40	217.30	46.95	2.87	3.53	3.69	0.30	0.20	0.37
PROPENE	91.37	96.88	82.84	41.00	33.91	33.24	1.22	1.66	2.06	0.00	0.28	0.38
ETHYNE	89.28	36.42	79.18	85.70	174.20	125.00	3.68	5.12	5.74	0.00	0.31	0.29
iBUTANE	91.07	36.46	81.60	97.60	34.10	119.20	2.27	1.90	1.66	0.10	0.16	0.09
nBUTANE	91.28	96.88	82.83	96.50	115.30	126.90	3.59	3.71	3.72	0.20	0.18	0.18
t2BUTENE	91.31	96.14	82.00	8.00	8.53	11.03	0.36	0.37	0.33	0.10	0.06	0.09
1BUTENE	91.13	95.54	82.32	7.60	7.05	7.88	0.21	0.23	0.21	0.00	0.01	0.01
c2BUTENE	91.35	96.24	82.73	6.20	5.87	5.17	0.20	0.20	0.18	0.00	0.02	0.03
iPENTANE	91.28	96.83	82.84	96.40	94.39	256.00	2.61	2.45	2.34	0.20	0.06	0.11
nPENTANE	91.35	96.86	82.80	23.20	17.69	58.21	0.67	0.54	0.62	0.00	0.02	0.03
13BDIENE	91.36	96.86	82.78	6.70	7.09	7.45	0.22	0.23	0.22	0.00	0.01	0.01
t2PENTEN	91.35	96.52	81.74	7.70	7.50	7.05	0.18	0.19	0.18	0.00	0.01	0.01
c2PENTEN	88.08	94.98	80.11	3.80	4.06	3.76	0.09	0.10	0.10	0.00	0.00	0.01
MEPENT	91.36	96.69	82.07	34.50	39.85	27.12	0.99	0.97	0.83	0.00	0.04	0.03
ISOPRENE	78.32	63.11	50.23	2.60	4.78	1.72	0.11	0.15	0.10	0.00	0.01	0.00
nHEXANE	91.11	63.13	79.55	8.00	7.70	4.79	0.26	0.31	0.24	0.00	0.02	0.01
nHEPTANE	91.35	92.13	84.07	5.10	6.16	3.10	0.19	0.15	0.13	0.00	0.00	0.01
BENZENE	91.89	95.23	85.67	30.30	33.77	29.14	1.03	1.04	1.02	0.10	0.08	0.06
TOLUENE	90.99	88.26	82.82	66.20	79.11	64.28	2.26	2.40	2.04	0.00	0.00	0.11
ETHBENZ	77.90	81.27	79.31	23.00	12.47	23.68	0.54	0.55	0.48	0.00	0.02	0.03
mpXYLENE	82.97	78.17	80.00	48.60	38.83	74.36	1.67	1.66	1.45	0.00	0.06	0.05
oXYLENE	37.97	70.75	66.86	17.30	16.05	19.29	0.88	0.56	0.48	0.00	0.02	0.02
9. CF	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	94.26	83.65	92.37	65.80	63.75	45.77	6.21	7.57	6.19	0.00	0.80	0.20
ETHENE	75.80	84.03	92.28	65.10	58.99	92.10	3.49	3.43	3.32	0.00	0.12	0.16
PROPANE	94.49	84.09	92.44	18.70	34.78	19.74	2.37	2.96	2.45	0.30	0.40	0.38
PROPENE	94.35	84.10	92.44	23.70	25.28	31.86	1.61	1.45	1.48	0.10	0.27	0.25
ETHYNE	90.66	38.22	68.84	62.30	88.12	57.23	2.86	3.40	4.10	0.10	0.23	0.18
iBUTANE	94.43	38.21	66.31	55.60	29.78	21.32	2.61	2.40	1.45	0.20	0.28	0.09
nBUTANE	94.43	84.09	92.41	83.10	113.50	93.26	4.38	4.02	4.00	0.10	0.25	0.21
t2BUTENE	94.50	83.89	92.35	9.50	3.59	4.75	0.75	0.27	0.20	0.10	0.03	0.03
1BUTENE	92.50	81.76	90.18	9.20	3.82	8.00	0.27	0.20	0.18	0.00	0.01	0.01
c2BUTENE	94.47	83.04	92.00	8.60	3.28	4.22	0.35	0.18	0.12	0.00	0.02	0.01
iPENTANE	94.34	84.09	92.43	54.90	74.04	95.14	3.53	3.07	2.86	0.20	0.19	0.13
nPENTANE	94.38	84.09	92.44	16.80	20.40	16.18	0.97	0.78	0.66	0.10	0.06	0.04
13BDIENE	94.12	83.70	92.07	10.10	7.20	6.45	0.27	0.23	0.22	0.00	0.01	0.01
t2PENTEN	93.58	84.00	91.96	4.90	5.03	6.35	0.22	0.20	0.21	0.00	0.01	0.01
c2PENTEN	93.88	83.42	91.50	6.60	2.70	3.47	0.15	0.10	0.11	0.00	0.00	0.00
MEPENT	94.35	83.57	92.20	30.50	25.45	41.69	1.58	1.23	1.10	0.00	0.06	0.05
ISOPRENE	78.28	66.70	89.85	19.60	3.01	3.42	0.13	0.13	0.11	0.00	0.00	0.01
nHEXANE	93.38	66.66	89.85	11.30	5.47	8.48	0.49	0.38	0.31	0.00	0.03	0.02

nHEPTANE	92.24	85.57	93.07	6.90	4.47	5.16	0.26	0.18	0.16	0.00	0.01	0.01
BENZENE	94.41	86.18	94.10	28.20	24.34	37.36	1.50	1.22	1.21	0.10	0.08	0.08
TOLUENE	93.71	85.66	94.09	49.10	49.06	78.92	2.42	2.12	2.17	0.10	0.11	0.08
ETHBENZ	65.90	71.93	88.26	14.70	8.27	13.37	0.48	0.40	0.40	0.00	0.02	0.02
mpXYLENE	85.46	72.50	86.82	29.70	27.17	41.59	1.28	1.29	1.21	0.00	0.05	0.04
oXYLENE	76.30	60.26	80.08	11.30	11.58	16.01	0.50	0.48	0.44	0.00	0.02	0.02

10. LP	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE		93.92	93.18		81.57	96.78		5.69	6.42		0.85	0.72
ETHENE		94.01	93.15		61.21	46.00		2.83	2.97		0.13	0.10
PROPANE		94.11	93.23		60.73	41.69		3.29	3.56		0.28	0.32
PROPENE		51.36	93.23		28.53	16.61		1.28	1.49		0.00	0.26
ETHYNE		93.68	73.62		139.90	90.36		4.89	4.01		0.15	0.12
iBUTANE		93.68	74.23		51.81	92.40		2.41	2.67		0.07	0.09
nBUTANE		94.09	93.23		118.20	172.70		5.25	5.15		0.14	0.13
t2BUTENE		51.29	78.40		5.90	5.46		0.35	0.28		0.04	0.03
1BUTENE		93.42	92.08		5.82	5.20		0.29	0.22		0.02	0.01
c2BUTENE		51.32	92.34		3.99	4.16		0.20	0.16		0.00	0.01
iPENTANE		94.04	93.23		42.58	70.09		2.61	2.40		0.07	0.05
nPENTANE		94.09	93.16		14.24	20.86		0.87	0.85		0.04	0.03
13BDIENE		94.06	92.54		6.45	3.53		0.21	0.21		0.00	0.01
t2PENTEN		93.56	91.47		5.71	7.67		0.26	0.21		0.01	0.01
c2PENTEN		91.29	87.56		2.64	3.56		0.12	0.10		0.01	0.00
MEPENT		93.89	93.03		16.77	16.96		0.86	0.78		0.02	0.02
ISOPRENE		73.31	41.53		2.18	0.88		0.11	0.07		0.00	0.00
nHEXANE		73.32	87.03		4.50	5.66		0.25	0.32		0.00	0.02
nHEPTANE		78.08	89.20		2.61	3.62		0.14	0.11		0.00	0.01
BENZENE		94.19	93.82		23.69	17.62		0.98	1.04		0.05	0.05
TOLUENE		87.18	90.11		39.67	39.51		2.12	2.00		0.09	0.08
ETHBENZ		91.88	88.72		7.52	6.77		0.37	0.38		0.02	0.02
mpXYLENE		92.02	92.99		25.87	23.00		1.19	1.13		0.05	0.04
oXYLENE		65.56	81.85		10.78	9.06		0.52	0.42		0.02	0.02

11. EH	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	82.39	87.11	80.82	57.70	84.43	122.50	3.47	4.23	4.43	0.20	0.37	0.76
ETHENE	82.28	87.01	80.81	32.70	105.70	46.48	1.85	1.95	1.91	0.00	0.08	0.12
PROPANE	82.26	87.02	82.40	99.30	351.00	553.30	2.15	3.37	3.87	0.10	0.17	0.23
PROPENE	82.36	87.03	78.01	11.90	16.22	13.73	0.66	1.00	0.87	0.00	0.14	0.19
ETHYNE	79.04	65.27	73.72	40.50	42.45	55.01	2.17	2.12	2.90	0.10	0.11	0.12
iBUTANE	82.34	65.32	74.99	85.40	35.96	120.10	1.77	1.55	1.50	0.00	0.05	0.04
nBUTANE	82.10	87.02	82.40	87.30	207.00	344.60	2.83	3.27	3.44	0.10	0.09	0.07
t2BUTENE	81.86	86.66	81.74	2.30	1.80	2.44	0.19	0.15	0.15	0.00	0.01	0.01
1BUTENE	77.75	83.85	81.28	2.50	2.78	2.47	0.15	0.13	0.12	0.00	0.01	0.01
c2BUTENE	79.97	83.63	78.16	2.00	1.29	1.88	0.12	0.09	0.08	0.00	0.01	0.01
iPENTANE	81.85	87.10	82.39	63.80	54.14	85.74	1.61	1.53	1.49	0.10	0.05	0.03
nPENTANE	81.82	87.02	82.38	65.40	62.60	99.88	0.75	0.76	0.79	0.00	0.02	0.01
13BDIENE	79.03	84.53	80.50	2.20	3.09	2.87	0.11	0.13	0.11	0.00	0.01	0.01
t2PENTEN	79.18	82.37	78.02	2.30	2.61	2.75	0.12	0.11	0.09	0.00	0.00	0.01
c2PENTEN	72.26	74.14	66.19	1.20	1.25	1.29	0.06	0.05	0.04	0.00	0.00	0.00
MEPENT	81.88	86.96	82.13	21.40	17.57	27.22	0.68	0.67	0.58	0.00	0.01	0.01
ISOPRENE	73.37	17.55		0.90	0.60		0.08	0.05		0.00	0.01	
nHEXANE	80.34	17.55	48.71	15.80	5.48	23.07	0.25	0.26	0.25	0.00	0.01	0.00
nHEPTANE	85.35	88.40	94.29	6.20	3.16	5.25	0.13	0.13	0.12	0.00	0.00	0.01
BENZENE	90.97	89.52	94.87	10.70	11.16	15.95	0.70	0.73	0.70	0.00	0.05	0.04
TOLUENE	89.06	86.58	71.71	27.40	26.57	16.63	1.56	1.59	1.28	0.10	0.05	0.04
ETHBENZ	81.67	63.47	55.36	9.00	4.42	14.41	0.26	0.34	0.31	0.00	0.02	0.04
mpXYLENE	79.27	63.96	64.44	13.90	13.45	44.31	0.75	1.02	0.82	0.00	0.07	0.04
oXYLENE	82.57	36.04	33.55	8.20	4.79	6.19	0.27	0.45	0.39	0.00	0.04	0.04

12. MD	%data capture			Max ppb			Mean ppb			Min ppb		
Compound	1994	1995	1996	1994	1995	1996	1994	1995	1996	1994	1995	1996
ETHANE	26.88	72.69	88.90	34.10	203.30	70.49	2.59	3.80	4.08	0.10	0.35	0.56
ETHENE	64.46	85.76	88.82	69.40	972.90	539.60	1.29	3.80	3.19	0.00	0.04	0.04
PROPANE	64.02	91.72	92.47	96.20	1142.00	290.70	4.62	5.61	4.96	0.00	0.34	0.36
PROPENE	64.52	14.26	19.13	67.80	49.83	95.93	2.04	1.58	6.07	0.00	0.20	2.02
ETHYNE	51.56	90.91	92.10	78.40	69.42	101.60	3.10	3.69	3.54	0.20	0.11	0.17
iBUTANE	53.70	90.92	92.13	91.00	234.50	44.98	3.86	1.75	1.57	0.10	0.09	0.06
nBUTANE	64.59	91.88	92.47	95.60	1152.00	291.00	7.23	4.48	3.46	0.10	0.15	0.12
t2BUTENE	64.71	91.53	92.00	56.70	42.18	10.90	0.60	0.19	0.20	0.10	0.00	0.04
1BUTENE	64.17	90.57	89.67	30.50	59.24	10.05	0.34	0.18	0.14	0.00	0.01	0.01
c2BUTENE	64.66	91.46	92.00	44.70	37.84	8.47	0.42	0.12	0.11	0.00	0.00	0.02
iPENTANE	63.57	91.85	92.47	92.20	414.90	163.40	4.15	2.05	1.61	0.10	0.07	0.05
nPENTANE	64.66	91.76	92.47	88.00	199.70	73.01	1.96	1.21	0.88	0.00	0.04	0.03
13BDIENE	63.32	91.23	91.87	7.50	83.07	9.17	0.26	0.27	0.18	0.00	0.01	0.01
t2PENTEN	64.65	91.18	88.79	26.80	34.97	6.11	0.49	0.16	0.13	0.00	0.00	0.01
c2PENTEN	62.23	87.09	81.00	13.80	19.23	3.06	0.28	0.07	0.06	0.00	0.00	0.01
MEPENT	64.81	91.23	92.20	75.70	76.95	40.44	1.89	0.72	0.62	0.00	0.02	0.02
ISOPRENE	41.85	75.75	37.93	10.20	3.17	1.19	0.18	0.09	0.07	0.00	0.00	0.01

nHEXANE	52.50	75.84	91.09	44.70	17.87	35.28	0.82	0.24	0.31	0.00	0.01	0.01
nHEPTANE	57.95	93.40	92.33	42.90	56.69	72.28	0.44	0.22	0.18	0.00	0.00	0.01
BENZENE	64.52	95.42	93.26	44.60	43.54	35.03	1.29	1.08	1.01	0.00	0.05	0.04
TOLUENE	55.65	93.62	93.28	31.60	41.48	37.56	2.63	1.65	1.49	0.00	0.09	0.05
ETHBENZ	50.27	88.18	90.63	63.50	14.05	6.41	0.78	0.36	0.31	0.00	0.01	0.02
mpXYLENE	52.18	88.58	91.48	22.60	19.25	15.12	1.70	0.97	0.82	0.00	0.03	0.03
oXYLENE	48.26	57.91	81.50	14.80	6.61	6.79	0.69	0.39	0.31	0.00	0.02	0.02

See Appendix 2 for site names.

iBUTANE	iso-butane
t2BUTENE	trans-2-butene
c2BUTENE	cis-2-butene
iPENTANE	iso-pentane
13BDIENE	1,3-butadiene
t2PENTEN	trans-2-pentene
c2PENTEN	cis-2-pentene
MEPENT	2 and 3 methyl pentane
ETHBENZ	ethylbenzene

Appendix 6:2 NPL Teddington data

Measurements are given in ppb unless otherwise indicated. * ≡ below detection limit

Sample collection date	28/10/87	26/11/87	21/12/87	23/2/88	25/3/88	24/5/88	13/7/88	22/9/88	24/11/88	26/1/89	15/3/89	5/11/89
Ethane	3.11	16.54	9.01	3.82	2.76	1.92	1.51	1.71	11.77	2.80	2.69	2.37
Ethene	4.48	3.21	4.02	3.64	2.46	1.31	1.12	0.57	24.87	1.93	1.27	1.36
Propane	2.07	25.12	8.68	11.42	1.40	1.71	1.12	1.83	22.08	3.30	2.45	2.68
Cyclopropane	*	*	*	*	*	*	*	*	*	*	*	*
Propene	2.30	2.13	2.88	8.51	3.16	5.56	5.40	0.97	10.93	2.38	1.32	1.64
2-methyl propane	1.99	11.45	3.92	2.64	0.81	0.71	0.66	0.56	18.95	2.08	3.67	1.55
Ethyne	4.38	2.82	2.77	*	0.68	0.79	0.79	1.05	34.89	3.37	1.78	1.44
n-Butane	4.77	28.93	8.55	3.54	1.96	1.37	1.44	1.15	33.85	3.78	4.40	1.96
Trans 2 butene	0.19	0.32	0.34	0.20	0.10	0.29	*	*	1.79	*	0.24	*
1-butene	0.73	0.59	0.58	0.93	0.46	0.55	0.45	0.19	2.42	0.44	0.36	0.30
2-methyl propene	*	*	*	*	*	*	*	*	*	*	*	*
2 2-dimethyl propane	0.61	1.04	2.15	1.13	0.87	0.83	0.99	0.50	2.93	0.94	0.98	0.95
Cis 2-butene	0.15	1.00	0.44	0.21	0.12	0.14	*	*	1.50	*	0.19	*
Cyclopentane	*	*	*	*	*	*	*	*	*	*	*	*
2-methyl butane	2.02	16.44	4.12	1.34	0.55	0.54	0.69	0.43	16.76	1.69	1.79	0.92
n-Pentane	1.23	16.07	3.33	0.79	0.51	0.60	0.46	0.50	8.91	1.00	0.66	0.47
1 3-butadiene	0.25	0.17	0.21	0.09	*	0.90	0.27	0.27	1.11	*	*	*
Trans 2-pentene	*	0.21	0.18	0.13	*	*	*	*	0.97	*	*	*
1-pentene	*	0.49	0.23	*	*	*	0.41	*	1.14	*	*	*
cis 2-pentene	0.43	0.27	0.23	0.21	*	0.39	*	*	0.84	*	0.28	*
2 3-dimethyl butane	*	*	*	*	*	*	*	4.74	1.54	2.11	2.90	1.49
2-methyl pentane	*	1.55	0.33	0.23	*	*	*	*	4.07	*	*	*
3-methyl pentane	*	3.34	0.98	*	*	*	*	*	3.54	*	*	*
n-Hexane	0.32	4.43	1.26	*	*	*	*	*	2.71	*	*	*
Isoprene	0.48	6.63	2.11	*	*	*	*	*	0.57	*	*	*
C7 aliphatic	*	*	*	*	*	*	*	*	*	*	*	*
n-Heptane	0.48	11.25	2.82	0.22	0.62	0.22	*	0.25	1.34	*	0.16	0.14
Benzene	2.93	27.83	2.61	0.84	0.19	0.60	0.55	0.32	9.08	1.08	0.63	0.80
2 2 4-trimethyl pentane	*	1.63	1.05	0.27	*	0.27	0.20	*	0.85	*	*	0.12
2 3 4-trimethyl pentane	*	20.39	0.18	0.08	*	0.15	*	*	2.71	*	0.42	*
3-ethyl hexane	*	17.71	0.19	0.23	*	0.14	0.31	0.08	1.51	*	0.08	*
n-Octane	*	32.41	1.82	*	*	0.26	0.38	*	*	*	*	0.58
Methyl benzene	12.01	112.22	4.87	1.30	0.72	0.67	0.29	0.29	19.36	1.50	0.75	0.81
n-Nonane	2.99	14.26	3.57	0.27	0.18	0.14	*	0.07	0.62	0.46	0.18	0.11
Ethyl benzene	0.83	1.47	0.80	0.97	0.86	0.83	0.62	0.38	4.16	5.32	1.50	0.47
1 4 & 1 3-dimethyl benzene	2.14	3.95	2.99	3.09	2.65	2.89	2.01	1.47	12.92	19.49	5.79	2.28
1 2-dimethyl benzene	0.27	1.23	0.82	1.07	0.93	1.04	0.62	0.20	4.13	2.50	0.70	0.30
1 3 5-trimethyl benzene	*	0.68	0.37	2.04	0.32	0.51	0.58	0.67	2.35	0.38	*	1.85
1 2 4-trimethyl benzene	0.19	1.14	3.51	0.66	0.33	0.27	0.38	0.23	2.31	0.60	*	*
Methane (ppm)	1.60	1.65	1.62	1.63	1.57	1.80	1.59	1.59	2.23	1.52	1.52	1.61
Unknown												
Total	52.95	390.57	83.54	51.50	24.21	27.40	22.84	20.02	271.71	58.67	36.71	26.20

Sample Collection Date	5/7/89	29/9/89	16/11/89	18/1/90	21/3/90	25/5/90	13/7/90	21/9/90	13/11/90	25/1/91	26/3/91	24/5/91
Ethane	2.09	3.12	3.66	2.47	2.31	1.91	1.68	1.31	1.98	5.59	4.10	2.88
Ethene	3.32	2.43	3.06	1.63	1.75	0.92	0.93	0.55	1.11	5.25	2.48	2.69
Propane	7.73	2.35	3.10	2.45	19.14	12.59	10.77	6.08	5.76	6.84	5.28	4.32
Cyclopropane	*	*	*	*	*	*	*	*	*	*	*	*
Propene	5.63	2.07	2.57	1.46	2.27	1.01	1.08	0.80	1.92	2.93	1.81	1.28
2-methyl propane	1.66	2.06	2.23	2.04	1.66	1.63	3.18	1.20	1.29	4.92	2.67	3.20
Ethyne	1.62	1.78	2.68	2.14	1.75	0.79	1.03	0.64	1.03	7.57	2.37	3.94
n-Butane	2.22	3.31	3.07	2.98	2.34	2.30	4.99	1.14	1.43	8.29	4.33	5.12
Trans 2 butene	0.23	0.19	0.16	0.14	0.13	0.11	0.12	0.11	*	0.36	0.22	0.15
1-butene	1.07	0.41	0.58	0.24	0.30	0.20	0.29	0.18	0.18	0.59	0.56	0.28
2-methyl propene	*	*	*	*	*	*	*	*	*	*	*	*
2 2-dimethyl propane	2.60	86.27	9.64	0.74	1.08	1.22	0.65	0.48	0.57	1.20	4.91	0.74
Cis 2-butene	0.22	0.13	0.17	0.12	0.12	*	0.12	*	*	0.34	0.21	0.14
Cyclopentane	*	*	*	*	*	*	*	*	*	*	*	*

2-methyl butane	1.41	1.88	1.37	1.12	1.15	1.17	2.57	0.68	0.78	4.09	2.37	3.08
n-Pentane	0.86	1.46	0.95	0.53	0.68	0.51	1.13	0.28	0.36	1.77	1.74	1.10
1 3-butadiene	0.06	8.53	0.31	*	0.26	*	0.13	*	0.13	0.33	*	0.24
Trans 2-pentene	*	*	0.13	*	*	*	*	*	*	0.27	*	*
1-pentene	0.88	0.14	0.38	*	*	*	0.16	*	*	0.31	*	*
cis 2-pentene	*	*	*	*	*	*	*	*	*	*	*	*
2 3-dimethyl butane	2.23	1.35	0.91	1.29	0.65	1.36	1.73	1.34	8.21	0.31	*	*
2-methyl pentane	*	0.30	*	*	*	*	0.30	*	*	0.94	0.29	0.35
3-methyl pentane	*	*	*	*	*	*	*	*	*	0.83	*	*
n-Hexane	*	0.34	*	*	*	*	*	*	*	0.70	0.66	*
Isoprene	*	*	*	*	*	*	*	*	*	*	*	*
C7 aliphatic	*	*	*	*	*	*	*	*	*	*	*	*
n-Heptane	0.23	0.17	0.33	*	0.17	*	0.18	*	0.16	0.34	0.46	0.17
Benzene	0.76	1.24	1.17	0.74	0.65	0.67	1.93	0.45	0.97	3.27	15.84	1.80
2 2 4-trimethyl pentane	0.30	0.57	0.12	*	0.14	*	*	*	*	0.58	0.12	0.18
2 3 4-trimethyl pentane	0.15	0.53	0.13	0.71	0.70	*	0.07	*	*	0.33	0.50	*
3-ethyl hexane	*	0.14	0.16	*	0.09	*	*	0.07	0.18	0.13	*	0.22
n-Octane	*	0.11	*	*	*	*	*	*	*	0.20	*	*
Methyl benzene	0.48	1.65	1.72	0.90	0.85	0.86	1.15	0.53	0.90	4.77	2.73	2.19
n-Nonane	0.37	0.18	0.16	0.19	0.23	0.15	0.10	0.09	*	0.24	0.61	0.19
Ethyl benzene	9.56	0.69	0.78	1.71	1.01	0.22	0.35	0.19	0.25	0.91	0.61	0.55
1 4 & 1 3-dimethyl benzene	35.95	2.74	2.92	7.47	5.06	0.57	1.15	0.56	1.09	2.72	2.16	1.76
1 2-dimethyl benzene	3.73	0.82	0.93	1.00	0.69	0.28	0.43	0.24	0.18	1.00	0.69	0.70
1 3 5-trimethyl benzene	*	0.14	0.47	1.24	1.43	1.19	0.61	0.30	0.33	0.28	1.04	0.29
1 2 4-trimethyl benzene	*	*	0.39	*	*	*	0.26	*	*	0.58	*	0.45
Methane (ppm)	1.54	1.73	1.74	1.55	1.54	1.56	1.52	1.57	1.60	1.77	1.71	1.65
Unknown	*	*	*	*	*	*						
Total	86.90	128.83	45.99	34.86	48.15	31.22	38.61	18.79	30.41	70.55	60.47	39.66

Sample Collection Date	11/7/91	19/9/91	29/11/91	21/1/92	24/3/92	27/5/92	27/7/92	23/9/92	26/11/92	28/01/93	26/03/93	24/5/93
Ethane	45.00	2.57	3.00	5.50	2.72	2.38	0.79	2.08	2.62	3.14	3.53	3.40
Ethene	18.89	5.12	2.83	4.30	1.31	0.94	0.42	1.52	1.54	2.39	1.98	1.44
Propane	7.57	5.79	2.39	5.07	1.79	1.99	0.70	1.42	5.04	2.28	2.01	1.85
Cyclopropane	*	*	*	*	*	*	*	*	1.33	1.24	*	*
Propene	37.48	2.93	1.66	1.89	1.18	0.80	0.33	0.85	0.84	1.17	0.69	0.86
2-methyl propane	3.40	4.44	1.59	2.71	1.02	1.82	1.57	1.03	13.45	3.31	2.26	3.13
Ethyne	1.25	6.49	2.65	2.64	1.31	1.63	0.76	2.01	1.82	2.88	3.24	2.29
n-Butane	4.77	8.54	2.85	4.86	1.90	3.06	1.94	2.07	14.00	4.54	4.51	5.85
Trans 2 butene	1.38	0.37	0.14	0.20	0.20	0.17	0.11	0.68	0.38	0.18	*	0.24
1-butene	6.36	0.58	0.37	0.35	0.32	0.17	0.12	0.30	0.24	0.24	0.13	0.34
2-methyl propene	*	*	*	*	*	*	*	*	*	*	*	*
2 2-dimethyl propane	35.81	1.17	0.86	1.33	0.67	0.48	0.41	0.31	0.39	0.39	0.94	0.74
Cis 2-butene	6.91	0.33	0.14	0.19	*	*	0.09	0.16	0.30	0.15	*	0.35
Cyclopentane	*	*	*	*	*	*	*	*	0.18	*	0.08	0.10
2-methyl butane	1.29	5.09	1.57	2.40	0.91	1.68	1.08	1.22	5.25	2.22	1.94	3.01
n-Pentane	0.58	1.78	0.67	1.23	0.51	0.80	0.31	0.64	1.15	0.63	0.70	1.00
1 3-butadiene	0.35	0.43	0.57	1.73	0.37	0.24	0.06	1.57	0.12	0.12	0.10	3.91
Trans 2-pentene	25.70	0.31	*	0.18	*	*	*	0.08	0.20	*	*	0.44
1-pentene	*	0.28	*	0.10	*	*	*	0.10	*	*	*	*
cis 2-pentene	1.25	0.17	*	*	*	*	*	0.13	*	*	*	0.29
2 3-dimethyl butane	2.81	0.25	*	*	*	*	*	*	*	*	*	*
2-methyl pentane	0.43	1.11	0.31	0.36	*	*	0.11	0.20	0.50	0.88	0.25	0.34
3-methyl pentane	0.41	0.91	*	*	*	*	0.14	0.31	0.33	*	0.36	0.29
n-Hexane	*	0.61	*	*	*	*	*	0.14	*	*	*	*
Isoprene	*	*	*	*	*	*	*	*	*	*	*	*
C7 aliphatic	*	*	*	*	*	*	*	*	*	*	*	*
n-Heptane	0.13	0.29	0.15	0.27	*	*	*	0.50	*	0.25	0.22	0.20
Benzene	1.44	2.63	0.99	1.74	0.76	0.79	0.35	0.60	0.85	0.93	0.98	0.95
2 2 4-trimethyl pentane	0.50	0.38	*	0.14	*	*	*	*	*	*	*	*
2 3 4-trimethyl pentane	0.09	0.19	0.17	*	*	*	*	0.05	*	*	*	*
3-ethyl hexane	0.51	*	*	*	*	*	*	*	*	*	*	*
n-Octane	0.80	*	*	0.21	0.11	*	*	*	*	*	*	*
Methyl benzene	1.95	5.13	1.42	2.88	0.68	0.95	0.38	0.78	0.99	4.00	1.37	1.13
n-Nonane	7.12	0.20	0.20	0.34	0.22	*	0.05	0.11	0.16	0.18	0.14	0.17
Ethyl benzene	0.23	2.41	0.40	0.78	0.26	0.35	0.12	0.42	0.36	0.47	0.35	1.19
1 4 & 1 3-dimethyl benzene	0.74	11.66	1.40	2.79	0.67	1.11	0.34	1.53	0.82	1.76	1.19	3.41
1 2-dimethyl benzene	0.22	8.64	0.46	0.90	0.27	0.52	0.14	1.36	0.27	0.49	0.54	0.61
1 3 5-trimethyl benzene	34.27	0.48	0.36	0.59	0.30	0.27	0.04	0.25	0.15	0.85	0.43	2.91
1 2 4-trimethyl benzene	*	0.81	0.18	0.39	0.28	0.23	0.26	0.06	0.22	0.93	0.28	0.30
Methane (ppm)	1.56	1.77	1.71	1.83	1.76	1.92	1.69	1.96	2.06	2.67	2.40	2.34
Unknown	*	*	*	*	*	0.12	*	2.14	1.48	2.11	0.67	2.46
Total	251.20	83.86	29.04	47.90	19.52	22.42	12.31	26.58	57.04	40.40	31.29	45.54

Sample Collection Date	30/7/93	30/7/93	30/9/93	30/09/93	30/11/93	10/01/94	24/1/94	09/02/94	24/2/94
Ethane	1.76	1.79	0.98	1.31	3.08	4.17	6.15	5.22	6.79
Ethene	1.32	1.04	0.56	0.35	2.84	2.95	8.44	7.05	5.91
Propane	0.73	0.46	0.33	0.37	1.29	5.22	2.70	2.86	3.75
Cyclopropane	2.25	*	4.14	*	0.41	0.09	0.08	*	*
Propene	0.52	0.29	0.47	0.12	0.89	1.00	2.69	2.22	1.57
2-methyl propane	0.99	0.77	0.23	0.22	0.99	1.14	6.01	3.54	2.68
Ethyne	1.23	0.85	0.30	0.31	2.49	2.84	*	13.18	9.69

n-Butane	2.30	1.57	0.54	0.47	3.06	1.68	17.86	7.15	5.32
Trans 2 butene	*	*	*	*	0.05	0.08	0.50	0.27	0.26
1-butene	0.10	0.06	0.07	*	0.13	0.20	0.49	0.37	0.63
2-methyl propene	*	*	*	*	*	*	*	*	0.61
2 2-dimethyl propane	0.12	0.08	0.10	0.06	0.40	*	1.02	1.13	*
Cis 2-butene	*	*	*	*	0.04	0.47	0.37	0.24	*
Cyclopentane	*	*	*	*	*	0.04	0.24	*	*
2-methyl butane	1.37	1.00	0.36	0.26	1.12	1.17	6.35	4.53	3.45
n-Pentane	0.42	0.28	0.19	0.10	0.37	0.51	1.49	1.21	1.56
1 3-butadiene	*	*	*	*	0.22	0.35	0.87	0.91	0.56
Trans 2-pentene	*	*	*	*	0.07	0.08	0.43	0.31	0.20
1-pentene	*	0.18	*	*	0.01	0.06	0.85	0.87	*0.38
cis 2-pentene	*	*	*	*	0.07	0.07	0.33	0.09	*
2 3-dimethyl butane	*	*	*	*	*	*	*	*	*0.50
2-methyl pentane	0.24	0.14	0.10	*	0.33	*	2.10	3.31	1.37
3-methyl pentane	*	*	*	*	0.15	0.90	0.82	0.69	0.61
n-Hexane	*	*	0.20	*	0.11	*	0.52	0.46	0.67
Isoprene	*	*	*	*	*	*	0.22	*	*
C7 aliphatic	*	*	*	*	*	*	*	*	0.48
n-Heptane	0.32	0.06	0.13	*	*	0.06	0.22	0.32	0.26
Benzene	1.09	0.57	1.12	0.50	0.07	0.72	2.51	2.20	2.13
2 2 4-trimethyl pentane	*	*	*	*	1.10	*	*	0.97	0.63
2 3 4-trimethyl pentane	*	*	*	*	*	*	*	*	*
3-ethyl hexane	*	*	*	*	*	*	*	*	*
n-Octane	*	*	*	*	*	*	*	*	*
Methyl benzene	1.34	0.57	1.29	0.30	1.12	1.01	3.45	3.94	3.16
n-Nonane	0.19	*	0.22	*	*	*	*	*	*
Ethyl benzene	0.36	0.10	0.30	0.09	0.38	0.22	0.39	1.24	0.68
1,4 & 1,3-dimethylbenzene	1.01	0.20	0.67	0.18	1.23	0.54	1.15	2.77	1.88
1 2-dimethyl benzene	0.28	0.12	0.27	0.10	1.52	0.17	0.51	1.15	0.67
1 3 5-trimethyl benzene	0.19	0.07	0.13	0.07	0.29	0.34	0.21	0.56	0.51
1 2 4-trimethyl benzene	0.16	0.09	0.05	0.12	0.59	0.17	0.08	1.65	0.64
Methane (ppm)	2.10	1.81	2.04	1.80	1.77	1.94	1.89	1.85	*
Unknown	2.89	0.51	3.39	0.08	*	*	*	*	*
Total	23.28	12.61	18.18	6.81	*	*	*	*	*

Sample collection date	10/01/94	24/01/94	09/02/94	24/2/94	11/03/94	18/4/94	06/05/94	20/05/94	02/06/94	15/06/94	15/06/94
Ethane	4.17	6.15	5.22	6.79	2.79	3.25	2.25	2.11	4.54	1.92	2.16
Ethene	2.95	8.44	7.05	5.91	1.03	1.23	1.24	2.14	0.95	0.68	0.86
Propane	5.22	2.70	2.86	3.75	1.18	1.33	0.82	0.98	1.38	0.70	1.00
Cyclopropane	0.09	0.08	*	*	*	*	*	*			
Propene	1.00	2.69	2.22	1.57	0.34	0.43	0.41	0.64	0.40	0.19	0.36
2-methyl propane	1.14	6.01	3.54	2.68	0.66	0.78	0.62	1.50	0.60	1.11	1.21
Ethyne	2.84	*	13.18	9.69	1.91	2.31	1.94	4.24	1.23	1.20	4.21
n-Butane	1.68	17.86	7.15	5.32	1.28	1.62	1.24	2.85	1.42	2.38	1.80
Trans 2 butene	0.08	0.50	0.27	0.26	*	0.05	0.03	0.05	0.04	0.03	0.05
1-butene	0.20	0.49	0.37	0.63	*	0.08	0.07	0.09	0.09	0.05	0.12
2-methyl propene	*	1.02	1.13	0.61	*	*	*	*	0.17	0.10	0.50
Cis 2-butene	0.47	0.37	0.24	*	*	0.05	*	*	*	*	*
Cyclopentane	0.04	0.24	*	*	*	*	*	*	*		
2-methyl butane	1.17	6.35	4.53	3.45	0.77	1.08	0.80	1.90	0.82	1.23	1.46
n-Pentane	0.51	1.49	1.21	1.56	0.27	0.43	0.24	0.46	0.29	0.28	0.42
1 3-butadiene	0.35	0.87	0.91	0.56	*	0.12	*	0.15	0.20	*	0.34
Trans 2-pentene	0.08	0.43	0.31	0.20	*	0.05	*	0.08	0.03	*	*
1-pentene	0.06	0.85	0.87	*0.38	*	*	*	*	*	*	*
cis 2-pentene	0.07	0.33	0.09	*	*	*	*	*	*	*	*
Cyclic C6	*	*	*	*	*	*	*	0.14	*	*	
2 3-dimethyl butane	*	*	*	*0.50	*	*	*	*	*	0.15	*
2-methyl pentane	*	2.10	3.31	1.37	*	0.38	0.27	0.71	0.20	0.27	0.34
3-methyl pentane	0.90	0.82	0.69	0.61	*	*	*	*	0.09	*	0.13
n-Hexane	*	0.52	0.46	0.67	*	0.13	0.06	0.14	0.10	0.07	0.16
Isoprene	*	0.22	*	*	*	*	*	*	*	0.17	*
C7 aliphatic HC	*	*	*	0.48	3.65	2.07*	*	5.00	13.86	*	
n-Heptane	0.06	0.22	0.32	0.26	*	*	*	*	*	*	*
Benzene	0.72	2.51	2.20	2.13	0.54	0.84	0.45	0.70	0.34	0.37	0.64
C8 aliphatic HC's	*	*	0.97	0.63	*	*	*	1.16	*	0.16	*
Methyl benzene	1.01	3.45	3.94	3.16	0.74	0.83	0.69	1.68	0.61	0.65	1.30
n-Nonane	*	*	*	*	*	*	*	*	*	*	*
Ethyl benzene	0.22	0.39	1.24	0.68	0.25	0.17	0.42	0.73	0.17	0.28	1.24
1 4 & 1 3-dimethyl benzene	0.54	1.15	2.77	1.88	0.44	0.48	0.70	1.06	0.36	0.49	2.01
1 2-dimethyl benzene	0.17	0.51	1.15	0.67	0.07	0.18	0.29	0.39	0.16	0.28	1.27
1 3 5-trimethyl benzene	0.34	0.21	0.56	0.51	0.58	*	*	*	*	*	*
1 2 4-trimethyl benzene	0.17	0.08	1.65	0.64	*	*	*	*	*	*	*
Methane (ppm)	1.94	1.89	1.85	2.34	2.01	2.63	2.39	2.11	1.97	2.25	2.00

Sample collection date	14/7/94	29/07/94	12/08/94	26/08/94	8/09/94	28/09/94	18/10/94	28/10/94	11/11/94	28/11/94	9/12/94	22/12/94
ethane	2.82	3.48	2.53	2.70	1.67	3.18	2.90	3.21	6.89	4.40	13.63	6.92
ethene	1.11	0.96	1.49	0.50	0.50	1.40	1.63	2.10	7.07	3.94	20.06	6.82
propane	0.87	1.20	1.11	0.67	0.47	1.02	1.42	1.37	4.23	2.51	6.58	4.70

cyclopropane	•	•	•	•	0.03	•	0.06	•	0.00	0.05	0.00	0.00
propene	0.28	0.39	0.48	0.17	0.21	0.43	0.46	0.62	1.98	1.35	5.95	2.40
iso-butane	1.00	0.74	0.69	0.52	0.17	1.01	0.90	1.08	3.57	2.69	8.94	3.94
n-butane	1.68	1.43	1.85	1.05	0.47	1.95	1.40	1.88	6.45	3.34	13.44	7.31
ethyne	1.75	1.48	1.58	0.43	0.32	0.96	2.39	3.14	10.19	11.26	58.87	10.10
trans-2-butene	0.05	0.02	0.05	0.05	0.04	0.07	0.05	0.07	0.26	0.21	0.89	0.29
1-butene	0.08	0.07	0.08	0.13	0.03	0.05	0.10	0.11	0.36	0.25	0.97	0.40
isobutene	0.33	0.20	0.15	•	0.10	0.16	0.40	0.24	0.69	0.46	2.00	0.68
cis-2-butene	•	•	•	•	•	0.03	0.05	0.07	0.22	0.17	0.74	0.42
cyclopentane	•	•	•	0.14	0.03	0.05	0.07	0.06	0.20	0.15	0.53	0.23
iso-pentane	1.18	0.89	0.95	0.68	0.28	1.24	1.10	1.29	4.71	3.24	12.43	4.73
n-pentane	0.29	0.27	0.30	0.20	0.09	0.32	0.36	0.37	1.38	1.06	3.22	1.30
1,3-Butadiene	•	0.23	0.13	•	0.12	0.13	0.19	0.14	0.84	0.60	2.66	1.12
trans-2-pentene	•	•	•	•	•	0.05	0.05	0.08	0.28	0.12	0.95	0.28
pentenes *	•	•	*0.07	0.05	0.05	0.09	0.24	0.29	0.92	0.93	3.87	1.01
cis-2-pentene	•	•	•	0.00	•	•	0.06	0.04	0.18	0.11	0.52	0.16
cyclic C6 *	•	0.08	•	0.10	0.12	•	0.24	0.34	1.20	0.88	3.59	1.23
dimethyl butane *	0.10	•	0.14	•	•	•	•	•	•	•	•	•
2-methyl pentane	0.28	0.14	0.23	0.13	0.06	0.22	0.30	0.30	1.03	0.76	3.13	1.05
3-methyl pentane	0.12	0.10	0.11	0.12	•	0.16	0.19	0.22	0.71	0.51	2.36	0.75
n-hexane	0.08	0.07	0.10	0.07	0.02	0.05	0.13	0.15	0.47	0.36	1.29	0.46
isoprene	0.33	0.24	•	0.06	•	•	0.06	0.02	•	0.18	0.48	•
C7 aliphatic HC *	•	•	2.27	0.60	3.49	8.26	0.34	0.29	3.34	15.25	8.66	1.13
n-heptane	•	•	•	0.03	0.03	0.02	0.10	0.11	0.28	0.24	0.73	0.37
benzene	0.39	0.38	0.42	0.28	0.17	0.47	0.46	1.22	1.97	2.30	5.82	1.92
C8 aliphatic HC *	0.20	16.01	0.22	0.20	0.06	0.10	0.26	0.40	1.38	1.17	5.40	1.73
toluene	0.71	0.62	1.05	1.75	0.37	1.03	1.17	1.32	3.43	2.77	11.42	4.56
C9	•	•	•	0.31	0.05	•	0.08	•	1.54	1.43	2.05	3.43
nonane	•	•	•	0.63	0.18	0.08	0.15	0.16	3.15	2.46	2.39	4.94
ethyl benzene	0.20	0.16	0.36	0.83	0.16	0.31	0.41	0.44	3.64	3.65	4.30	4.59
m-p xylene	0.31	0.22	0.64	1.12	0.27	0.55	0.74	1.01	4.82	4.79	8.89	4.58
o-xylene	0.11	0.09	0.21	0.66	0.10	0.20	0.32	0.42	2.35	1.92	4.09	2.32
1,3,5-trimethyl benzene	0.52	•	•	2.57	0.38	0.32	0.49	0.41	1.15	1.52	0.86	0.53
1,2,4-trimethyl benzene	0.31	•	•	0.23	0.14	0.29	0.52	0.25	0.87	0.56	0.99	0.33
C10	•	•	•	6.17	0.35	0.41	1.18	1.41	42.03	48.43	32.63	32.36
Methane conc. (ppm)	1.82	1.91	1.97	1.88	1.90	1.91	1.93	1.93	2.14	2.00	2.26	2.07

Sample collection date	06/01/95	20/01/95	03/02/95	17/02/95	29/03/95	21/04/95	28/04/95	17/05/95	31/05/95	27/06/95
ethane	6.15	2.51	2.50	2.60	3.00	3.29	3.24	2.28	2.46	2.04
ethene	7.30	1.08	1.44	1.48	0.96	1.37	1.72	1.14	1.57	1.14
propane	3.33	1.34	1.33	1.23	1.40	3.08	1.04	0.84	0.71	1.20
cyclopropane	•	•	•	•	•	0.63	•	0.46	•	•
propene	2.38	0.36	0.48	0.43	0.40	•	0.42	•	0.42	0.42
iso-butane	3.66	0.58	0.85	0.44	0.82	2.28	1.20	0.39	0.91	1.50
n-butane	6.28	0.66	1.73	0.88	1.46	4.06	1.51	0.87	1.44	2.88
ethyne	14.49	3.80	1.97	1.73	2.87	2.50	3.34	1.66	2.04	1.47
trans-2-butene	0.52	0.05	0.06	0.04	0.07	•	•	•	0.08	0.09
1-butene	0.45	0.08	0.11	0.06	0.08	0.32	0.03	•	0.08	0.12
isobutene	0.81	0.18	0.19	0.14	0.20	0.22	0.18	•	0.35	0.26
cis-2-butene	0.33	0.05	0.05	0.05	0.06	•	•	•	0.07	0.09
cyclopentane	0.19	0.04	0.13	0.02	0.04	•	0.04	•	•	0.14
iso-pentane	4.45	0.69	0.91	0.52	0.89	2.89	1.70	0.69	1.62	2.63
n-pentane	1.15	0.29	0.31	0.20	0.29	1.16	0.40	0.25	0.39	0.54
1,3-Butadiene	1.23	0.23	0.21	0.23	0.11	•	0.07	•	0.16	0.12
trans-2-pentene	0.37	0.03	0.05	0.03	0.05	•	0.04	•	0.10	0.10
pentenes *	1.19	0.06	0.16	0.07	0.16	•	0.18	0.10	0.37	0.39
cis-2-pentene	0.21	0.03	0.03	0.02	0.04	•	0.01	•	0.05	0.05
sat. C6	1.30	0.18	0.28	0.10	0.17	0.63	0.35	•	0.45	0.62
dimethyl butane *	•	•	•	•	•	•	•	•	•	•
2-methyl pentane	1.21	0.17	0.22	0.11	0.23	0.60	0.35	•	1.46	0.43
3-methyl pentane	0.84	0.11	0.14	0.08	0.13	0.41	0.22	•	0.35	0.28
n-hexane	0.51	0.11	0.13	0.05	0.08	0.32	0.16	•	0.17	0.16
isoprene	0.22	•	•	•	0.18	0.09	•	•	0.30	0.21
Sat C7s	13.55	0.16	0.11	15.67	6.03	3.72	0.23	8.66	0.46	7.54
n-heptane	0.33	0.07	0.09	0.05	•	0.23	0.18	•	0.12	0.11
benzene	2.38	0.43	0.45	0.48	0.50	1.00	0.94	0.68	0.83	0.55
C8 aliphatic HC *	1.33	0.04	0.19	0.06	0.22	0.14	0.19	•	0.30	0.28
n-octane	0.16	0.08	•	•	•	•	0.14	•	0.37	•
toluene	4.63	0.71	0.69	0.68	0.80	1.86	1.64	0.61	1.22	1.01
C9	0.26	0.36	0.07	•	0.03	•	•	•	•	•
nonane	0.90	1.62	0.58	0.19	0.23	0.24	0.63	•	0.12	0.05
ethyl benzene	1.47	1.70	0.65	0.37	0.21	0.51	0.91	0.25	0.26	0.14
m-p xylene	3.19	1.28	0.66	0.44	0.48	0.97	1.50	0.53	0.70	0.27
o-xylene	1.35	0.52	0.29	0.15	0.20	0.36	0.86	0.22	0.29	0.10
1,3,5-trimethyl benzene	•	•	•	•	•	0.76	•	•	•	•
1,2,4-trimethyl benzene	•	•	•	•	•	0.54	•	•	•	•
C10	7.81	9.46	3.36	3.33	2.05	0.71	5.68	•	0.85	0.18
Methane conc. (ppm)	2.18	1.90	1.86	1.90	1.94	•	•	•	•	•